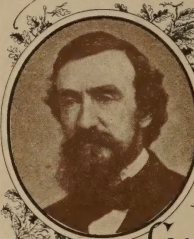


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THE CHEMISTRY OF
PAINTS, PIGMENTS AND VARNISHES

THE CHEMISTRY OF PAINTS, PIGMENTS & VARNISHES

BY

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NEW YORK
VAN NOSTRAND COMPANY
EIGHT WARREN STREET

1924

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PREFACE

IN few industries of comparable size and importance were scientific methods applied so late as in the Paint and Varnish Industry, and in none has the value of these methods been more clearly demonstrated. To-day the industry is one of the most highly specialised: empirical methods of manufacture have been superseded by processes based on detailed research work by trained specialists; many new raw materials have been introduced; and, in the different branches of the industry, the attack on the many and fascinating problems presented is being pursued constantly and scientifically. Numerous difficulties which baffled the patience and skill of the earlier chemists have been overcome. To instance a few of these, the Lake manufacturer has now at his command a range of synthetic dye-stuffs of a permanency and colour stability undreamed of twenty-five years ago; new and more efficient solvents have been discovered; celluloid and nitro-cellulose lacquers have been introduced; methods of application by spraying and dipping have been perfected, and the synthetic production, on a commercial basis, of artificial resins seems to be in sight.

These are but a few of the more important of recent developments, and it has become a matter of no small difficulty for those interested in the industry to keep abreast with the numerous new processes. The "Chemistry of Paints, Pigments and Varnishes" has been written in the hope that it will be of assistance to works managers and to students in obtaining both a general survey of the industry as a whole and an account of the modern technical processes and of the chemistry of the raw materials employed. In addition to those actually engaged in the different branches of the industry, I trust that it will be found useful also to analysts called upon to test these materials, and to architects and others who have to specify them for various protective uses. With this object detailed methods of analysis have been given, and the specifications included will enable users of the materials to judge whether various products and specialities offered to them reach the standard required and are suitable for the purpose in view.

It will be understood that it has not been possible, nor was it the intention, to include in a book of this nature more than a brief description of the different types of machinery involved. Any reader desirous of obtaining more detailed

information on these matters is referred to the authorities mentioned in the Bibliography at the end of the book.

I am indebted to Mr Alwyne Meade, the author of "Modern Gasworks Practice," for much valuable advice and encouragement in the preparation of this book, and to the manufacturers noted in the text who have kindly furnished illustrations. In conclusion I have to express my thanks to my brother, Mr James Bearn, who has given me great assistance in revising the text.

J. G. B.

LONDON, *October* 1923

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THE CHEMISTRY OF PAINTS, PIGMENTS AND VARNISHES

PART I

Paints : Their Composition, Properties and Uses

CHAPTER I

INTRODUCTORY

PAINTS may be defined generally as liquids which contain solid particles in suspension, and which are used both as protective and decorative coatings on the surfaces to which they are applied.

Paints are usually made by grinding the solid particles or pigments in an oil or varnish medium to an extremely fine state of sub-division, a small proportion of a volatile "thinner," such as turpentine, being added in order that the paints may be spread easily and uniformly.

The paint medium or vehicle commonly used is composed of a mixture of raw and boiled linseed oil, for raw linseed oil if used alone would dry too slowly to be satisfactory.

The rate of drying of paints may, if desired, be accelerated by the addition of driers such as sugar of lead (lead acetate) and borate of manganese (see Chapter XX.).

When paints are applied the volatile medium evaporates, leaving behind an oil pigment coating, which dries or hardens owing to the absorption of oxygen from the air by the oil content. The solidified oil acts as a binder for the pigments and holds them in their place.

The addition of varnish, such as copal varnish, causes the paints to dry off with a bright glossy surface ; when so treated these paints are known as enamel paints, or simply as enamels.

Besides being sold in the "ready-mixed" or liquid state ready for use, paints are also made in the paste form by grinding the pigments in raw linseed oil.

Colours ground in oil are prepared for use by thinning down with a suitable paint medium composed of raw and boiled linseed oil, with the addition of turpentine and a small percentage of driers.

Sometimes dry colours are described as paints, and specifications are met with in which they are described under this designation, as, for example, "Paint, Chinese

Blue, Dry." The use of the word "paint" in this way is to be deprecated, for it is better to describe all such dry colours as pigments.

An exception may, perhaps, be made in the case of mixed pigments containing driers and made to some particular shade or pattern, as, for instance, "Khaki Paint, Dry," with a mixture of, say, white lead, yellow ochre, carbon black, red oxide, and which simply requires mixing with a proportion of liquid medium to make it ready for use.

A paint when applied in the form of a thin film or coating should dry off in a reasonable time, say 8-12 hours, giving tough, elastic, hard and durable coatings.

A good quality of paint should be easily applied, cover well, be opaque, or, as it is generally described, possess good "body"; it should also be durable on exposure, so that it may afford suitable protection to the surfaces to which it is applied.

Paints may also be made to dry with a matt or semi-matt (egg-shell) finish by decreasing the amount of oil or varnish content and increasing the proportion of volatile thinners.

The body and covering power of a paint is dependent on the amount and nature of the pigments it contains in suspension; and as a rule the finer the state of sub-division of the particles of the pigment the greater the body and covering power.

The durability of a paint is dependent on the nature of the oil or oil varnish content, and only pure drying oils should be used in their preparation.

The addition of rosin or other soft resin varnish mediums will cause the rapid deterioration of paint films on exposure to weathering influences, resulting in the paints cracking and chipping off after only a few months' exposure.

Paint films wear better than oil films, as the latter are somewhat porous, and the addition of the pigments tends to make them dry off harder and become more impervious to air and moisture.

Additions of polymerised oils such as blown oils and stand oils to paint mediums increase their durability to a remarkable extent, owing to the fact that such films on oxidation give highly elastic and waterproof films. The same result is also obtained by judicious admixtures of hard copal varnishes and wood oils.

The protective and anti-corrosive properties of paints vary enormously according to their composition. As a rule coloured paints, such as red oxide paints, carbon black paints, etc., are found to be more durable than white or light-coloured paints.

The durability of a paint as regards its protective and wearing properties can only be determined by practical exposure tests lasting over several years.

It has been found that paints containing alkaline or basic pigments and those containing chromates are the most efficient in protecting iron-work from corrosion, whilst those containing mixtures of white lead and zinc oxide pigments are remarkable for their extreme durability and hard-wearing properties.

The addition of the so-called inert pigments as "extenders" to paint, such as barytes, silica, and whiting, was formerly looked upon purely and simply as the addition of adulterants, but it has been shown as regards some of them that they

tend to prolong the life of the paint, and are valuable adjuncts provided they are used in limited amounts.

Paints on exposure over a period of years may chalk, checker, crack, blister, or shell off; the original colour of the paint may also change or even completely disappear. A high-class durable paint for outdoor use should wear well over four or five years, retain its colour, and chalk only to a moderate degree, so that on washing down a good surface remains for repainting.

Paints which blister or crack are unsatisfactory, inasmuch as it is necessary to remove completely all the loose and badly adhering paint before any repainting can be done.

In order to get a clear insight into the nature and properties of paints it is essential to have an accurate and clear knowledge of the physical and chemical properties of the components used in their preparation.

The chemistry of the pigments will be found fully described in Part II. of this book, and that of the liquid mediums in Part III.

CHAPTER II

MANUFACTURE OF PAINTS

PAINTS are composed of :—

- (1) Pigments,
- (2) Oil or Oil Varnish Mediums,
- (3) Turpentine or other volatile spirits,
- (4) Driers,

which are incorporated together in suitable proportions so that the resultant product may be easily applied and dry off with a hard and durable surface. The chief operations involved in the process of manufacture are pugging, grinding and mixing.

PUGGING

The pigments selected must be carefully tested to ensure that they are of uniform fineness and free from coarse particles ; if there is any doubt about this they should be sieved through fine wire sieves in sifting machines specially made for the purpose.

The pugging machine (Fig. 1) consists of a large, vertical, cylindrical iron vessel provided with a powerful stirrer fitted with blades and mechanically operated.

The fine pigments are carefully weighed out and a portion emptied into the pug together with a little oil—usually raw linseed oil.

The stirrer is set revolving, and gradually more and more pigment is added together with the oil until the whole is taken up, only sufficient oil being used as is necessary to convert the pigments into a very stiff paste. The amount of oil measured out and added to the pug is carefully noted. It is important to see that no more oil is used than is required to form a stiff paste.

The pug is emptied by raising a slide at the bottom, the motion of the revolving blades forcing the pasty mass out into a pan placed in position to receive it.

GRINDING

(1) ROLLER MILLS

The paint paste is next ground through a triple roller mill (Fig. 2), which is now usually electrically driven. The roller grinding mills are made in various sizes, and the rolls may be made of either granite or chilled steel.

The space between the rollers may be regulated at will so that any degree of

fineness of grinding may be obtained. The middle roller has a lateral motion imparted to it whereby more efficient grinding is secured.

The pasty material is introduced between the first two rollers, and a steel scraper takes off the ground material as it issues from the end roller.

The paint is usually put through the mill two or three times, but where especially fine grinding is required it is necessary to put the material through the roller many times; towards the end of the operation the mill is screwed up very tightly so as to get the maximum grinding effect.

Combination pug and roller mills are also made whereby the pugging and grinding operation can be carried out simultaneously.

(2) EDGE RUNNER MILLS

Pigments may also be ground to paste form in edge runner mills in cases where a high degree of fineness is not essential, as, for example, in the manufacture of putty (whiting ground stiff in linseed oil) and paste driers.

An edge runner mill (Fig. 3) consists of a circular basin-shaped iron trough which is fixed and on the bed of which the pigments and oil to be ground are placed.

The grinding is done by means of a circular stone or steel runner set edgewise and fitted with gearing which causes it to run round the pan or bed of the mill.

Many types of edge runner mills are made; the type in common use has two vertical runners provided with scrapers to prevent the material from caking on the bottom of the mill and to turn it constantly over so that effective mixing and grinding is obtained.

(3) FLAT STONE GRINDING MILLS

Flat stone grinding mills are extensively used for grinding pigments in water, and also in turpentine for making the so-called "turps colours."

They are very slow, but grind extremely efficiently, and hence are still employed in the manufacture of gold-size colours for coach-work, and for colours in oil such as graining colours like siennas, umbers, Vandyke brown, etc., where an extremely fine product is required.

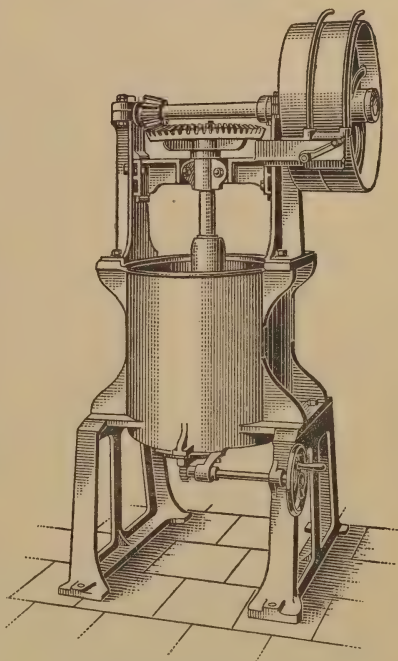


FIG. 1.—VERTICAL PUG MILL.
(Follows & Bate, Ltd.)

This type of mill consists simply of two heavy circular flat stones placed on top of one another, the faces of which are cut into grooves so as to increase the grinding power of the stones. The lower stone is fixed, while the other is made to rotate over the other. The material to be ground is fed from a hopper through a circular hole cut in the upper stone, and passes as it is ground outwards to the edge and falls into a pan.

The flat stones are usually made of granite; French burr or other types of hard stones may be used.

The Americans have introduced mills of this type in which the stones are replaced by grooved chilled steel and fitted with a cold-water cooling arrangement.

These types of mills are very useful for grinding coach colours in oil or turpentine, as the cooling arrangement prevents any overheating which would cause discoloration or loss of turpentine by volatilisation.

(4) CONE MILLS

Cone mills are largely used in the manufacture of enamels, and are very economical in use, as a battery of twelve or more of them can be worked by one man; further, only a moderate power is required to drive them.

Cone mills may be arranged horizontally, but they are usually vertical. The grinding edges may be either of stone or, as is more usual, of steel, the grinding surface edge of which is deeply grooved (see Fig. 4).

The mixture of pigments and varnish is emptied into the cone mill in a state of thin consistency, and the mill screwed up so as to regulate the flow of the ground liquid to ensure that the required degree of fineness of grinding is obtained.

Usually the materials need to be run two or three times through the mill to obtain the necessary degree of fineness. The ground enamel is then sieved and is ready for use.

MIXING MACHINERY

The paste colours ground in oil are thinned down for use—that is to say, made into ready-mixed paints in paint-mixing machines.

Various machines of this type are made, the simplest form of which consists of a pan into which can be lowered a paddle which is made to revolve at a moderate speed (see Fig. 5).

The stiff ground paint is weighed out and introduced into the pan with a proportion of the paint medium. The paddle is then lowered into the pan and set revolving.

As the paint mixes with the medium more and more of the latter is added till the paint is reduced to the right consistency, when it is run out through strainers and is ready for use.

A full description of the special machinery used in the manufacture of paints is outside the scope of this book, and the reader who is desirous of such information is referred to the special works dealing with this subject (see Bibliography).

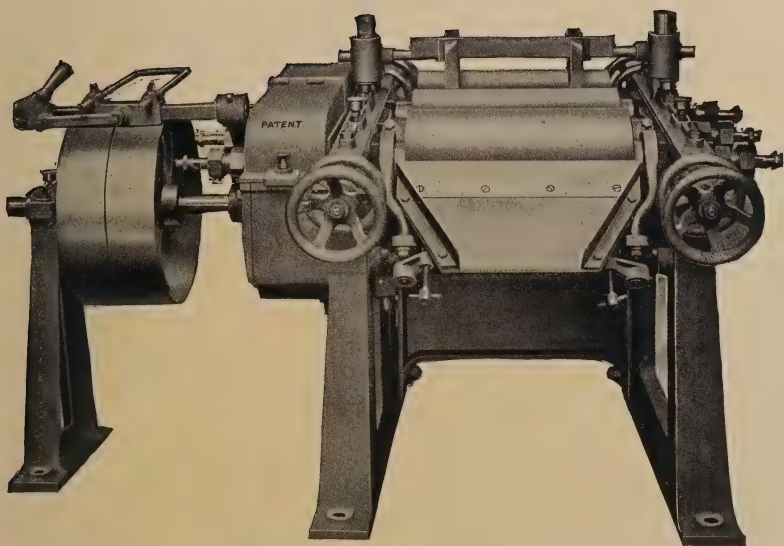


FIG. 2.—TRIPLE ROLLER MILL. (Torrance & Sons.)

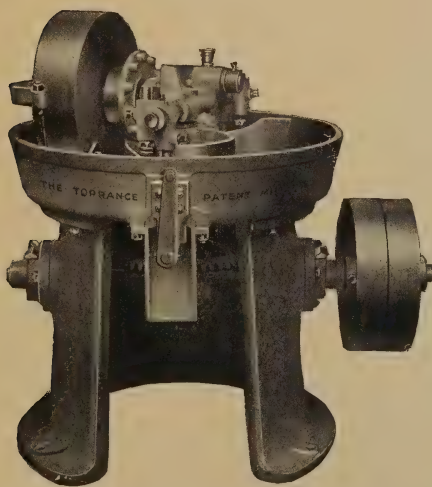


FIG. 3.—IRON EDGE RUNNER MILL. (Torrance & Sons.)

CHAPTER III

WHITE AND COLOURED PAINTS, ENAMELS, ANTI-CORROSIVE AND ANTI-FOULING PAINTS

IN this chapter a description is given of the various paints which are in common use for protective and decorative purposes, together with a general survey of their properties and the various purposes for which they are used.

PASTE COLOURS

Colours in oil are pigments ground to a pasty consistency in raw linseed oil which require thinning down with various paint mediums in order to make them ready for use.

These paste colours may consist of genuine pigments—which is usually the case with the strong staining colours such as the umbers, ochres, siennas, etc.—or, as happens with the great majority of paste colours which are sold, of genuine pigments mixed with cheap inert bases or extenders, such as barytes, Paris white, and so on; such paste colours are sold as No. 1, 2 or 3 qualities, according to the amount of reduction.

The amount of oil required to grind a pigment to a pasty condition varies to an enormous extent according to the specific gravity of the particular pigment. The white pigments, such as white lead, zinc oxide, etc., are ground in refined oil in order that discoloration of the pigment may be avoided. Usually a trace of ultramarine blue or Prussian blue is introduced during the grinding operation with a view to improving the colour of the finished product.

Coloured paints, especially those made from the slow-drying pigments such as carbon black, purple oxides, etc., are ground with a proportion of boiled oil so as to improve their drying properties; a small amount of varnish or boiled oil foots is incorporated with the grinding oil in order that the pigments may grip the rollers better during the grinding operation, thus admitting of their being more finely ground and giving the finished product a smoother and more pleasing appearance.

In the case of some of the paste colours it is customary to place a little water on the top of the casks in which they are stored to prevent skinning. Where the use of water would be objectionable oil paper should be used.

READY-MIXED PAINTS

About fifty years ago the quantity of ready-mixed paints sold was comparatively small, the painter preferring to buy the paste colours and thin them down himself to the right consistency. In recent years, however, there has been an increasing demand for ready-mixed paints, and at the present time an enormous trade has sprung up in them. This is, no doubt, chiefly due to the labour saved in thinning down the paste colours, but also partly to the introduction of special paint mediums by firms engaged in the trade, whereby these paints are endowed with properties vastly superior to those of the product obtained by the painter with the ordinary mediums at his disposal.

Paste colours are usually thinned down with an oil mixture consisting of four parts of boiled oil (pale boiled oil in the case of white and light-tinted colours) and one part of turpentine to the right working consistency, a small proportion of terebene or paste driers being stirred in to improve the drying properties of the paint.

With many of the high-class ready-mixed proprietary paints special mediums are used, as has been mentioned above, for thinning the paste colours, as well as special machinery, so that a thorough incorporation of all the products takes place.

The special mediums generally used by the paint manufacturer consist of a mixture of polymerised oils and elastic varnishes such as the copal varnishes, whereby special durable and hard-wearing properties are imparted to the finished paints.

In recent years, owing to the high price of turpentine, various substitutes such as white spirits (see Chapter XVII.) have been used with satisfactory results, and it is quite likely, owing to the depletion of the American pine forests and the consequent increasing price of turpentine, that before long white spirit will eventually supersede the American spirits of turpentine as the volatile constituent in all ready-mixed paints.

The paste and liquid driers employed in the manufacture of liquid paints to accelerate their drying qualities consist of the salts or oxides of lead cobalt and manganese, for a full description of which the reader is referred to the chapter on driers (Chapter XX.).

The ready-mixed cheap paints so largely sold in small packages (1 and 2 lb. tins) for amateur use are as a general rule of very poor quality on account of the large amount of weighting material such as barytes which they contain; for this reason they are usually coarse and deficient as regards body and covering power.

ENAMEL PAINTS, ENAMELS OR JAPANS

Enamel paints, especially white enamel paints, are exceedingly popular at the present time because of the beautiful, lustrous, highly-polished surfaces obtained by their use.

These full-gloss paints are made by grinding the pure pigments extremely finely (zinc oxide usually in the case of white enamels) in the requisite quantity of a mixture of stand oil and copal varnish.

As a rule enamels dry rather slowly, especially those made with a large amount of stand oil, requiring sometimes as long as twelve to eighteen hours before they are surface dry. They possess excellent body and covering power, and as a consequence of their tough and elastic nature are exceedingly durable, wear well, and retain their gloss for a long period under the severest exposure tests.

White enamels are sometimes made by grinding zinc oxide in pale dammar varnish; the enamel so made is extremely white in colour, but owing to its brittle nature is suitable only for indoor use.

No definite proportions can be given for the amount of oil varnish mixture required to a given weight of pigment, as this naturally varies considerably according to the nature of the pigment or pigments used in its manufacture.

Flat Enamels.—Enamels may also be manufactured so that they dry with a flat or matt finish; sometimes with a half-gloss or egg-shell finish, according to the purpose for which they are intended.

Flat or half-gloss enamels are made in exactly the same way as the full-gloss enamels, but the proportion of the varnish used to pigment is decreased whilst the amount of turpentine is increased. Sometimes a proportion of wax may be added so as to produce the desired flattening result.

Flatted enamels are largely used as flat wall finishes and for general indoor decoration, and for this purpose they are much superior to distempers (see Chapter IV.) on account of the permanency and beauty of finish which characterise them. Further, they can be easily washed down when required without in any way spoiling the beauty of the surface of the enamel. These paints are usually “stippled” with the object of imparting to them a soft velvet finish. On account of the comparatively small amount of varnish used in their preparation they are not suitable for outdoor use unless protected with a coat of varnish.

Quick-drying Varnish Paints and Enamels, Petrifying Liquids.—Quick-drying varnish paints are usually prepared by grinding the pigments in sharp-drying rosin or oil rosin varnishes. They dry off as a rule in an hour or two with a glossy surface.

These varnish paints are generally a cheap line of goods, and are only suitable for painting toys, furniture and such like, and for internal work generally, for owing to their rosin content they soon become brittle and crack and shell off when exposed to weathering influences.

Care should be taken to use only those pigments which do not thicken up or liver (“feed up”) with rosin varnishes, otherwise the paints would quickly set up solid in the containers and be rendered unfit for use.

Speaking broadly, hardened rosin varnishes are used in their preparation—that is to say, varnishes in which the rosin acids have been neutralised by zinc oxide or lime (see Chapter XVIII.). White petrifying liquids, for example, are often made by dissolving up rosin in white spirit or naphtha and running the hot solution on to zinc oxide, ground to a paste in linseed oil, and stirring well. Vigorous action takes place, due to the combination of a portion of the zinc oxide with the rosin, and when the reaction is over the white petrifying enamel is run through sieves into containers and is ready for use.

Petrifying liquids, whether coloured or transparent, for outdoor use require to be made from copal varnishes to withstand the severe weathering conditions to which they are liable to be exposed.

Gold-size Colours.—Colours bound in gold size are pigments which have been ground to a paste form in quick-drying gold size, *e.g.* shellac gold size; they are extensively used by coach painters as body colours. They dry off very quickly, giving hard flat surfaces which can be easily rubbed down and over which varnishes are applied so as to get the desired finish.

In the manufacture of gold-size colours only pure pigments or lakes should be used, and it is essential that the grinding should be as near perfection as possible.

For many purposes the pigments are ground in turpentine (turpentine colours), a little gold size being afterwards added by the painter to produce the desired binding effect.

AGRICULTURAL AND IMPLEMENT PAINTS, DIPPING AND SPRAYING PAINTS

Paints used for agricultural machinery, etc., may be quick-drying gold-size colours which require varnishing; but as a general rule it is found more convenient to use enamel paints which are made of hard-wearing copal varnishes; these dry off with glossy surfaces, wear well, and retain their colour and gloss under all weathering conditions. They are usually supplied to the manufacturers of agricultural machinery in a thin liquid condition so that they may be applied by spraying or by the dipping process.

The dipping and spraying processes have come rapidly into favour in recent years owing to the rapidity and ease with which they can be used, and the great saving of labour effected in applying paints and varnishes as compared with the brush method.

STAINING AND GRAINING COLOURS

Strong staining colours consisting of such pigments as siennas, umbers, Van-dyke brown, yellow ochre, and so on, ground to a paste form in linseed oil, are extensively used by painters for obtaining the various tints required in their work.

By the skilful use of these colours the expert painter is enabled to produce remarkably good imitations of mahogany, oak, walnut, etc., out of ordinary white wood.

The processes of glazing and scumbling, in which one colour is superimposed on another, permits the experienced artist to produce those beautiful effects that are familiar to all.

ANTI-CORROSION PAINTS

The protection of ironwork from corrosion by means of specially prepared paints has occupied the attention of paint chemists for many years, and an immense number of experimental practical trials has been carried out at various times in an endeavour to elucidate this very important problem.

Sir Robert Hadfield has estimated that the annual loss caused by the corrosion of iron and steel amounts to no less a figure than twenty-nine million tons.

Various bitumen preparations made from asphaltum, coal tar pitch, etc., in conjunction with a proportion of boiled oil—such as the well-known Dr Angus Smith's bitumastic composition—have been in use now for many years, and have been found to give most excellent results.

It has also been found, after a long series of practical trials (many of which have been carried out in America), that those pigments which inhibit corrosion may be divided into two classes, viz., those which are alkaline or basic, and those which comprise the chromates, the latter group owing its value in this respect to the well-known power of chromic acid to act on nascent hydrogen and to induce the "passive state" in iron.

The pigment in most general use as a priming or first coat for iron structures such as bridges is red lead, which is a basic pigment possessing anti-corrosive properties which are beyond dispute.

Red lead when mixed in oil, as is common knowledge, tends to set up hard, and for this reason requires to be used soon after mixing. Recently, however, brands of red lead (free from litharge) have been placed on the market which are non-setting and which may be mixed in oil and kept an indefinite time without undergoing any perceptible thickening or setting up.

Graphite and ferri-silicon paints have also been found to have excellent anti-corrosive properties, and are largely used for painting ironwork.

The medium used with such pigments as red lead, graphite, etc., is most commonly boiled oil, though it has been found that the addition of polymerised oils such as stand oils and treated wood oils (see Chapter XVI.) to the boiled oil tends to prolong the life of the paint and also at the same time to cause the paint films to be more impervious to moisture.

Paints made from lead and zinc chromes have also been found by practical tests to possess excellent anti-corrosive qualities, though their general use for this purpose has, on account of their comparative costliness, not been adopted to any great extent.

Red oxide of iron paints, as well as paints made from black oxide of iron and carbon black, are, by reason of their cheapness and first-rate anti-corrosive properties, very largely employed for the protection of iron and wood surfaces, and on the whole with very satisfactory results.

Anti-corrosion paints that are used as a protective and first coating on ships' bottoms are usually made from a strong oxide of iron (containing not less than 80 per cent. Fe_2O_3) ground in a quick-drying oil dammar varnish, and thinned out with low flash shale naphtha.

ANTI-FOULING COMPOSITIONS

Anti-fouling paints are used on ships' bottoms in order to prevent the growth of barnacles and weeds.

They are as a general rule quick-drying iron oxide paints to which a proportion

of poisonous material has been added, the amount of poisonous substance being greater in the case of ships sailing in tropical waters, where of course the growth of weeds and barnacles is much more rapid than in the colder regions.

The poisonous materials used are white arsenic, mercury oxide, finely precipitated sub-oxide of copper (Cu_2O), copper sulphocyanide, emerald green, copper sulphate, Scheele's green, verdigris, etc.

The medium used in their preparation is a gum oil varnish, containing a proportion of rosin and thinned down with shale naphtha so that the paints will dry off rapidly and thus allow the painting work to be expeditiously carried out.

Anti-fouling compositions are sometimes made by mixing the poisonous material with a wax basis, which requires to be melted and "clagged" on hot by the aid of trowels.

In painting a ship's bottom two coats of anti-corrosive priming and one coat of anti-fouling composition are applied. The majority of anti-fouling compositions are of a dark red colour, but occasionally green anti-fouling compositions are met with, the colouring matter in this case being a mixture of emerald and mineral green.

The following analysis by the author of some of the well-known anti-fouling compositions which are in common use will give a general idea of the composition of these paints :—

(1) FOR TROPICAL WATERS

Pigment	43·10 per cent.
Oil, resin mixture	30·20 „
Shale spirit	26·70 „
	<hr/>
	100·00

The oil and gum mixture contained 8 per cent. of free rosin. The resinsates consisted of equal parts of zinc and copper resinate.

Analysis of Pigment

Ferric oxide (Fe_2O_3)	22·54 per cent.
Sub-oxide of copper (Cu_2O)	34·20 „
Copper sulphocyanide (CuCnS)	14·41 „
Mercury oxide (HgO)	15·12 „
White arsenic (As_2O_3)	3·00 „
Lime (CaO)	2·06 „
Zinc oxide (ZnO)	1·56 „
Sulphur trioxide (SO_3)	1·53 „
Sodium sulphate (Na_2SO_4)	1·86 „
Insoluble matter	1·59 „
Moisture and alkalies	2·13 „
	<hr/>
	100·00

(2) Pigment	42.70 per cent.
Oil, gum resinate	29.10 „
Shale naphtha	28.20 „
	<hr/>
	100.00

The oil, gum resinate was of a greenish colour and an analysis of the ash gave—

Copper oxide (CuO)	4.01 per cent.
Zinc oxide (ZnO)	2.30 „

Analysis of Pigment

Sub-oxide of copper (Cu ₂ O)	32.58 per cent.
Ferric oxide (Fe ₂ O ₃)	34.10 „
Oxide of mercury (HgO)	9.11 „
Calcium sulphate (CaSO ₄)	11.47 „
Silica (SiO ₂)	8.80 „
Magnesium oxide (MgO)	1.18 „
Calcium chloride (CaCl ₂)	1.26 „
Moisture	1.50 „
	<hr/>
	100.00

(3) COLD WATER ANTI-FOULING COMPOSITIONS

Pigment	36.31 per cent.
Rosin, etc.	36.90 „
Shale spirit	26.79 „
	<hr/>
	100.00

The varnish residue contains 73 per cent. of free rosin, the remainder being calcium resinate. The resinates contain 6 per cent. of arsenic.

Analysis of Pigment

Ferric oxide (Fe ₂ O ₃)	56.00 per cent.
White arsenic (As ₂ O ₃)	21.16 „
Zinc oxide (ZnO)	1.01 „
Mercury oxide (HgO)	6.88 „
Calcium sulphate (CaSO ₄)	12.25 „
Silica (SiO ₂)	2.70 „
	<hr/>
	100.00

(4) Pigment	26.50 per cent.
Shale spirit	25.10 „
Resinates	48.40 „
	<hr/>
	100.00

The resinates consist chiefly of zinc resinate.

Analysis of Pigment

Silica (SiO_2)	4.76 per cent.
Ferric oxide (Fe_2O_3)	30.46 „
Zinc oxide (ZnO)	25.00 „
Copper Sulphate (CuSO_4)	19.59 „
White arsenic (As_2O_3)	11.38 „
Mercuric oxide (HgO)	5.39 „
Calcium sulphate (CaSO_4)	3.42 „
	<hr/>
	100.00

As an immense variety of paint products are manufactured for different industrial uses, both in the paste and the ready-mixed form, it would be quite impossible, as will be readily understood, to give a detailed description of them all with their diverse properties, but it is hoped that the description given above will indicate in general outline the methods in vogue for their preparation, as well as their composition.

It will of course be understood that paints used in the neighbourhood of gas works and acid works require to be made with pigments which are unaffected by sulphuretted hydrogen (which precludes the use of white lead) and acid fumes, and also that the mediums in which the pigments are ground should on drying give tough and impervious films highly resistant to all chemical agencies.

White paints made for hot-houses should be made on a zinc oxide basis, as white lead paints are often found to develop rose-coloured spots over their surface, due to the growth of a paint-destroying fungus.

As the appearance of these red spots has often been a source of mystification even to experienced paint technologists, the following interesting account, taken from Gardner's "Paint Researches and their Practical Application" (Washington, D.C., pp. 276-7), may be cited as throwing valuable light on the subject:—

"Among the most remarkable of fungi is one that elects to grow on fresh paint. It flourishes in the greatest profusion in hot-houses, its development being apparently favoured by a high temperature and constant humidity, as it is but rarely observed on paint elsewhere. About a month or two after a hot-house has been painted, more especially if white paint has been used, numerous small, rose-coloured specks appear on the paint; these specks gradually increase in size and change to a purple or sometimes dark red colour, suggesting the idea of blood

having been spread over the paint. In course of time the discoloured areas extend considerably and form broadly-effused patches several inches across. About a week after the coloured patches are fully developed their surface becomes studded with minute blackish-red warts. Each wart is a fungous fruit, containing myriads of very minute spores, which in due course are dispersed and start new points of infection.

“When the spores of the fungus are sown on a streak of wet white paint, a faint roseate tint appears in about a week's time, and within three weeks fruit is produced in abundance, and the deep purple characteristic blotches are well developed. Spores sown on a thin smear of pure linseed oil germinate as readily as in paint, but the mycelium remains colourless, and so far, no fruit has been produced. The result is the same when the spores germinate in ordinary nutritive media or in water. No germination takes place when the spores are sown on a streak of pure white lead or carbonate of lead (pigment). Hence this substance alone is not a suitable medium for the growth of the fungus, although its presence is necessary to enable the paint to complete its normal course of development, and it is also the constituent from which the fungus produces as a by-product the purple-red colouring matter which is collected in oily-looking drops within the cells of the mycelium, the cell walls themselves remaining colourless. The red colour suggests that the white carbonate of lead undergoes some chemical change induced by the presence of the fungus, resulting in the formation of red oxide of lead. This matter, however, requires careful investigation. The presence of 2 per cent. of carbolic acid in paint completely arrests the development of the fungus.”

METALLIC PAINTS

Metallic paints, such as aluminium and gold paints, are extensively used on account of their anti-corrosive and highly decorative properties. They are prepared by simply mixing the finely powdered metals or their alloys with suitable varnish mediums.

The metals must be in an exceedingly fine state of subdivision, and are manufactured by special processes involving the use of intricate grinding machinery.

The mediums used may be either thin copal varnishes or celluloid varnishes, the latter being preferable on account of their neutral and colourless properties.

Aluminium paints are made by stirring in about 3 lbs. of the fine metallic powder—as free from grease as possible—into 1 gallon of the medium and mixing well.

Gold paints are made in the same way as aluminium paints, various shades being obtained according to the particular colour of the gold or bronze powder used.

Various coloured effects may also be obtained by mixing different coloured aniline dyestuffs with the metallic paints, giving us green, blue, yellow, etc., coloured metallic paints.

As the gold and bronze powders have a much greater specific gravity than

that of aluminium, much more of them will be required to the gallon of medium, roughly about 6 lbs. to the gallon being necessary.

Since copal varnishes ordinarily contain acids from the copal gums used in their manufacture, care must be taken to neutralise them with lime, zinc, oxide, etc., before use as metallic paint mediums, otherwise they would act on the metallic powders; turning them green in the case of the gold powders and thus spoiling the colour of the paint; whilst in the case of aluminium powders hydrogen may be evolved.

LUMINOUS PAINTS

The commercial sulphides of calcium, barium and strontium possess the properties of appearing luminous ("phosphoresce") in the dark, after being previously exposed to light, and are used in the manufacture of luminous paints. The light emitted gradually diminishes in intensity, but on re-exposing the compound to the light, its luminosity is restored.

This singular property has been long known, and calcium sulphide (CaS) was formerly termed "Cantous phosphorus," and barium sulphide (BaS) "Bononian" (*i.e.* Bolognian) phosphorus.

Balmain's luminous paint, which is the best known of these products, is a sulphurous combination of calcium made by the aid of a high degree of heat.

The pure sulphides do not phosphoresce, so that this property would appear to be attributable to the presence of minute quantities of foreign substances. Traces of other elements, such as bismuth, cadmium, manganese, etc., modify the colour of the phosphorescent glow.

These alkaline earth sulphides are converted into paint form by mixing with gum arabic solution or a gum dammar varnish medium. Acidic varnishes such as copal varnishes containing lead driers cannot be used, as they would destroy the sulphides.

Radio-active luminous paints, which are used for painting watches, compasses, etc., differ from the formerly known phosphorescent substances in the fact that they do not require any prior exposure to light. On the contrary the action is in this case produced permanently by the rays which are thrown off by the radio-active substances such as mesothorium and radiothorium used in their preparation.

CHAPTER IV

DISTEMPERS, COLD WATER PAINTS

WASHABLE Distempers, or cold water paints, are in great demand at the present time on account of their comparative cheapness, and also because of the large range of shades in which they are made and the beauty of the matt finish obtained by their aid.

Washable distempers are manufactured either in the form of a thick paste or jelly, or in powder form.

DRY DISTEMPERS

These distempers (called Kalsomines in America) are sold in two forms—those which require to be mixed with hot water to develop their adhesive properties, and those which are prepared for use simply by the addition of cold water.

Cold water distempers usually contain casein as the binding agent in association with alkalies or alkaline earths. On the addition of cold water the alkali is dissolved and acts as a solvent for the casein.

Sometimes dextrine, or finely powdered glue which has been previously treated so as to render it soluble with cold water, may be used in place of casein.

The coatings furnished by these casein distempers dry quickly, giving matt or flat surfaces which, after a few days' exposure to the air, become insoluble and adhere so firmly that they may be lightly sponged over without washing off. On account of the firmness of the adhesion and insolubility of these paints it is possible to apply a second coat of distemper a few hours after the first coat has dried, a property which is very valuable in cases where two or three coats are necessary in order to completely hide the surface which is being painted.

These paint surfaces are usually stippled so as to hide all brush marks that might otherwise be in evidence, and also to give the surface a matt velvet-like finish.

In addition to the binding constituents, these paint powders contain one or more of the following materials: whiting, China clay, terra alba, lime, etc., together with the necessary tinting colours.

Whiting is undoubtedly the best white base for distempers, as it possesses excellent body and whiteness in water (oil, on the other hand, turns it a dirty transparent grey colour), and is superior in this respect to either terra alba or China clay, which are much more transparent. As a rule, however, a proportion of China clay or terra alba is used in conjunction with the whiting in order to improve the flowing power and ease of application of the finished paint.

The pigments used for tinting the distempers must be permanent and perfectly fast to lime and alkalis. Consequently such colours as Prussian blue, vermilionettes, lead chromes, cannot be used, and in their place pigments such as ultramarine blue (also alum-resisting), Lithol red, Hansa yellow, etc., must be substituted.

In hot water dry distempers the binding agent is powdered glue or size. In this case no alkali is necessary, as the size readily dissolves on the addition of hot water.

Size distempers are, generally speaking, not so washable as those made with casein, so that on applying a second coat there is a tendency for it to work up the under coat, which spoils the finished surface of the paint. To avoid this trouble it is customary to add a small proportion of some hardening agent, such as bichromate of potash, formaldehyde, stearate of lime, alum, etc., so that the paint surfaces on exposure to air and light dry off with more or less insoluble films or surfaces.

The pigment used in the tinting of distempers should always be first tested in lime and dilute alkaline solutions to see that they are quite permanent to these agents, otherwise the distemper may be rendered useless. This is especially desirable in the case of many of the lime greens which are sold as being fast to lime, but are found on testing, even after only a few days' exposure, to completely fade away.

Dry cold water paints are manufactured by grinding the colours, etc., in an edge runner and adding the casein, or glue binder, in sufficient quantity to fix properly the pigment and bases used. Great care must be taken to see that all the materials used are thoroughly dry before being incorporated together, as even a small portion of moisture present would cause the powder to cake and set up into hard lumps, and, of course, render it useless.

A little boric acid, salicylic acid, aluminium sulphate or other dry preservative is added to keep the dry powder sweet and prevent any decomposition that might take place on standing.

The powder should be ground very finely and sifted through special sifting machinery in order to get the necessary sub-division of the particles and their intimate admixture (see Fig. 6).

The dry distempers are then packed in waterproof containers, and should be stored in a dry place, as in a moist atmosphere rapid deterioration would take place.

PASTE DISTEMPERS

These are manufactured by grinding together pigments such as lithopone, zinc oxide, Paris white, blanc-fixé, etc., in a special medium which on cooling sets to a jelly-like consistency. These paste distemper grinding mediums are made by dissolving glue in hot water and thoroughly incorporating a proportion of linseed oil or a wood oil varnish till an emulsion is formed.

A small percentage of liquid carbolic acid, boric acid or formaldehyde is added as a preservative to keep the distemper sweet, otherwise on storage it would go mouldy and decompose.

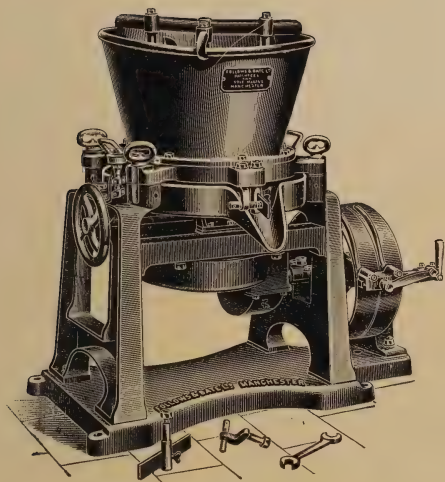


FIG. 4.—CONE PAINT MILL.
(Follows & Bate, Ltd.)

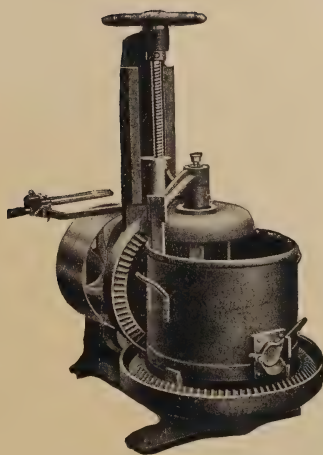


FIG. 5.—LIQUID PAINT MIXER.
(Torrance & Sons.)

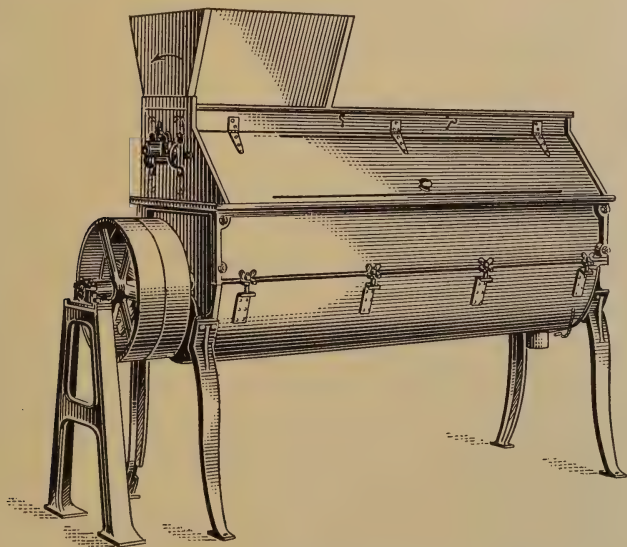


FIG. 6.—GARDNER'S COMBINED RAPID SIFTER AND MIXER.

Sometimes casein dissolved in alkaline solution is used in place of the glue as the binding agent.

The pigments used to tint these distempers must be fast to lime, as in the case of the powder distempers.

Paste distempers are made ready for use simply by adding sufficient hot water to reduce them to a creamy consistency. The pigment content of white paste distempers usually contains 30 per cent. of lithopone and 70 per cent. of Paris white, which is ground in a 10 per cent. solution of glue containing about 15 per cent. of oil or varnish mixed with it. A little ultramarine blue is added to increase the whiteness of the finished product.

A little alum may be used to act as a hardening agent, and sometime Irish moss is mixed with the glue solution in order to improve the brushing and laying-on properties.

The bright red distempers are prepared from aniline lake pigments fast to lime, such as Para or Lithol red precipitated on Paris white, whilst the greens are made from basic aniline dye-stuffs such as brilliant green or malachite green on green earth. The yellow pigments used may be either ochres, zinc chromes, or Hansa yellow struck on Paris white. Other tints may be obtained by the use of ultramarine blue, siennas, umbers, Venetian reds, and so on.

The following recipes (taken from Scherer) will give the reader a general idea as to the composition of these distempers made with casein as the binding agent.

(1) *Dry White Distemper.*

	Parts by Weight.
Casein, soluble in alkali . . .	100
Caustic lime from marble . . .	100
Levigated chalk (whiting) . . .	800
Borax	1
Ultramarine	2 to 2½

(2) *Dry Stone Distemper.*

Parts.
10
10
40
1
Ochre 40

(3) *White Paste Distemper.*

	Parts by Weight.
Casein	144
Slaked lime	7
Spanish white	280
Water	160

(4) *Coloured Dry Distempers.*

	Parts by Weight.
Casein	45
Powdered slaked lime . . .	20
Kaolin	150
Whiting	300
Lime fast pigments accord- ing to colour desired	5 to 20

PROPERTIES AND USES OF DISTEMPERS

Distempers should readily thin down to suitable brush consistency on the addition of the necessary amount of water. They should possess good body and covering power, and brush on easily without any pull. On drying off, the surface

should show no signs of streakiness or brush marks and should be a perfectly flat finish.

The tints should be permanent and the ready-mixed distemper should be free from any offensive odour, and should retain its sweetness even after it has been mixed for several days.

The distemper should second coat soon after the first coat has dried on without working up or in any way interfering with the first coat. The finished distemper when dry should adhere firmly to the surface to which it is applied and not scale or rub off; it should also withstand washing with water.

Distempers are often used in place of oil paints as a cheap priming paint on wood, plaster and stone surfaces in order to lessen the cost; the resulting smooth level surface thus obtained lends itself admirably to the subsequent application of oil paints.

As has already been stated, distempers are very largely used as a cheap flat wall paint in place of wall paper, and are extremely popular on account of their sanitary properties and the beautiful matt effects which may be obtained by the judicious use of the many tints which are available.

ANALYSIS OF DISTEMPERS

The analysis of a distemper is a comparatively simple matter; as a rule a simple qualitative analysis being all that is necessary. The base, which usually consists of one or more of the following materials—Paris white, China clay, terra alba, zinc oxide and lithopone, together with the necessary tinting colours—may be determined by the usual analytical methods.

The percentage of casein or glue used as the binding agent may be estimated by making a nitrogen determination by the well-known Kjeldahl method. The presence of an alkali will indicate that casein has been used in its manufacture; if absent it may pretty generally be inferred that glue is the binding agent.

FIREPROOF PAINTS

Paints manufactured as a protective coating to wooden structures in order to render them fireproof may be divided into two classes—first, those that have an oil vehicle, and secondly, those made with a distemper medium.

The base usually employed is finely powdered asbestos, which is tinted with the necessary pigments which must be impervious to heat. A small proportion of chemical salts, such as alum, tungstate of soda, ammonium phosphate, etc., which possess the property of preventing inflammability are also ground into the paint.

A medium made up with silicate of soda solution and casein possesses valuable fireproof properties and is superior in this respect to those mediums made up from either oils or a glue solution.

A first coating or priming solution, consisting of an aqueous solution of sulphate of alumina or ammonium sulphate, is usually first applied to the wood and allowed to soak in and dry before applying the subsequent coats of fireproof paint.

CHAPTER V

THE ANALYSIS AND VALUATION OF PAINTS AND ENAMELS

THE analysis of paints and enamels as regards their chemical composition and physical properties is a matter of the utmost importance, as it is only by means of a very careful and systematic examination of these products that an accurate estimation of their value can be deduced.

CHEMICAL ANALYSIS

Separation of the Vehicle.—In the chemical analysis of a paint it is necessary first of all to separate the vehicle from the pigment. This may be done by extracting the vehicle in a Soxhlet's (Fig. 7) or other convenient extraction apparatus, using either acetone or other suitable solvent as the extracting agent.

A very easy and convenient method of separating the medium from a paint so as to obtain the dry pigment consists in weighing out about 5-10 grams of the sample in a tall narrow beaker and adding 50 c.c. of petroleum ether, stirring well and leaving a few hours to settle. The top clear liquid is then decanted off through a double weighed filter paper into a weighed conical flask. The extraction process is repeated three or four times, and in the last one, acetone or benzol may be used in place of the petroleum ether in order to obtain a more perfect extraction. The pigments are then washed on to the filter paper, dried and weighed.

The amount of oil or oil varnish is obtained by distilling off the solvent extract and weighing the residue.

Another very convenient method for separating the vehicle from the pigment is by centrifuging the paint in a centrifugal machine.

The amount of the volatile constituent in a ready-mixed paint is estimated by distilling off 100 grams or more of the sample and collecting the distillate, or (more roughly) by heating on a sand bath and weighing the residue after all the volatile matter has been driven off.

ANALYSIS OF THE PAINT VEHICLE

The paint vehicle may be either a mixture of raw and boiled oils thinned with turpentine, white spirit, naphtha, or other volatile solvent, or it may consist of a

rosin or a gum varnish, or mixtures of both, with or without the addition of linseed oil.

The nature of the separated medium in which the pigments were ground may be readily ascertained by pouring a few drops of it on to a sheet of glass and examining the film obtained on drying. A mixture of raw and boiled linseed oils will give a softish film which dries in about twelve hours, whilst a rosin or oil varnish will dry more rapidly, giving tough and highly lustrous films, due to their resin or rosin content.

The presence of rosin in the vehicle may be determined by the Lieberman-Storch test for rosin (see page 162).

If the vehicle consists of linseed oil, its freedom from mineral oil may be ascertained by adding three drops to an alcoholic potash solution, boiling well, and then adding distilled water. The solution should remain perfectly clear, any turbidity indicating the presence of unsaponifiable matter (mineral oil).

If the medium consists only of linseed oil (or other drying oils) a determination of its specific gravity, iodine value, etc., may be carried out according to the usual procedure for the analysis of oils (see Chapter XVI.) in order to determine its exact composition.

If rosin varnishes or gum varnishes are present then the nature and the amount of resin and oil present may be estimated by the ordinary methods adopted for the analysis of oil varnishes (see Chapter XVIII.).

The volatile constituents driven off are usually turpentine or white spirit, and should be fractionated in order to decide their composition, though as a general rule the smell will suffice to give a good idea respecting their nature.

A portion of the vehicle should be burnt off and the residue examined in order to determine the amount and nature of the soluble driers that have been used in its preparation (see Chapter XX.).

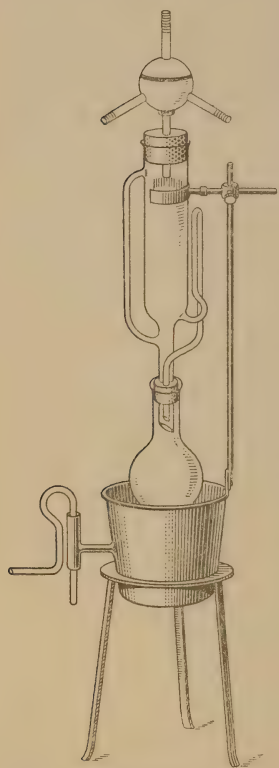


FIG. 7.—SOXHLET'S EXTRACTION APPARATUS.

ANALYSIS OF THE PIGMENTS

The dry pigment or pigments obtained after the removal of the vehicle should first of all be qualitatively analysed with a view to deciding their nature

and the approximate quantities present. By this preliminary analysis much time will be subsequently saved when the quantitative estimation is carried out, as the analyst will then be in a position to draw up a scheme of analysis suitable for the particular dry material under examination.

The quantitative analysis of the pigments separated from a paint offers no particular difficulties, and is carried out according to the usual schemes of analysis, descriptions of which will be found under the various chapters devoted to the chemistry of the different pigments commonly used in the manufacture of paints.

WHITE PAINTS

The pigments used in the manufacture of white paints are usually white lead, zinc oxide and lithopone, though occasionally white oxide of antimony and titanium oxide may be met with.

These pigments may be used alone, or mixed together in suitable proportions in the pure state; but as a general rule they are associated with inert bases or extenders such as barytes, Paris white, terra alba, silica and china clay, which are added in various proportions to reduce the cost of the paint.

COLOURED PAINTS

The composition of coloured paints is a much more complicated matter than that of the white paints on account of the large range of pigments that may be used in their preparation; also on account of the fact that the same or nearly the same coloured paints may often be produced by entirely different combinations of colour pigment.

A brief indication of the colour pigments present in the more commonly used coloured paints will give a general idea of the composition of the latter. It will, of course, be understood that besides these colour pigments it is usual to add as extenders, in order to reduce the cost of the paint, inert bases such as barytes, Paris white, etc.

Black Paints.—Carbon black, vegetable black, black oxide of iron, ivory black, lamp black, graphite.

Red Oxide Paints.—Red oxide of iron, Venetian red, Tuscan red, Turkey red oxide, Indian red.

Bright Red Paints.—Vermilion, vermilionettes, para red, alizarine lakes, lithol red, helio fast red, and other aniline red dye-stuffs precipitated on suitable bases.

Blue Paints.—Ultramarine, Prussian blue, Brunswick blue, cobalt blue, aniline blues (Methylene Blue Lake, etc.).

Yellow Paints.—Lead chrome yellow, zinc chrome, ochres, aniline yellow lakes such as Hansa yellow, lithol yellow, etc.

Green Paints.—Brunswick greens, green oxide of chromium, zinc greens. Also aniline greens such as malachite green, brilliant green, etc., precipitated on a green earth or other base.

Brown Paints.—Umber, Vandyke brown.

Purple Oxide Paints.—Purple oxide of iron.

The various tinted paints which are obtained by the addition of small amounts of different pigments to a white base such as white lead or zinc oxide are innumerable, and no useful purpose would be served by attempting to enumerate them. The reader who is interested in the subject is referred to the special works dealing with the subject of Paint and Colour Mixing (see Bibliography).

ESTIMATION OF WATER IN PAINTS

Ready-mixed paints usually contain a small proportion of water in order to prevent the pigments present from settling out hard in the containers on long standing. The amount of water used varies from 1 to 3 per cent., and so long as this proportion is not exceeded its addition is beneficial inasmuch as ready-mixed paints, especially those which are exported, are often packed for months or even years before they are used. If water were not added the paint would set to a hard mass at the bottom of the containers and be rendered practically useless.

Some manufacturers employ various patent emulsifying agents in place of water such as glue solutions, solutions of common salt, soda carbonate, sugar of lead and the like.

Whiting, China clay, and blanc-fixé (precipitated barytes) are often used in place of ordinary barytes with the heavier pigments on account of their non-settling properties, which helps to keep the pigments in suspension and prevent them settling out hard in the containers.

The addition of a small percentage of glycerine has also been found to be very useful in preventing settling in ready-mixed paints, as also the "livering" of certain pigments, *e.g.* Prussian blue when ground in oil.

The presence of water in a paint may be detected by rubbing it on a white porcelain slab with a little eosin dye-stuff. If water is present the eosin will be turned a pinkish colour, otherwise no change will be apparent.

PHYSICAL TESTS

The quantitative analysis of a paint will give very valuable information as to the nature and quantity of the pigments and vehicle which have been used in its preparation, but this requires to be supplemented by a series of thorough, practical tests if we are to gain an insight into its value as a protective coating for the various purposes for which it is to be used.

The value of a paint is judged according to the following properties :—

- (1) Fineness.
- (2) Consistency and working qualities.
- (3) Body.
- (4) Covering power.
- (5) Time of drying.
- (6) Nature of the dry surface ; its durability and wearing properties.

The practical testing out of the paint should be carried out in the following manner:—

A series of pink primed boards about 30 inches long and 12 inches in width are prepared by giving them two coats of a hard drying pink priming paint and rubbing down well after each coat.

The paints to be tested are stirred well up so as to get a thorough admixture of all the ingredients, and applied with a clean brush, care being taken to lay on the paint evenly, and remembering that two thin coats are as a general rule preferable to one thick coat.

The consistency and working properties of each paint should be carefully noted, and also a comparison made as to their opacity (body) and covering power.

If an accurate comparison of the body and covering power is required, then the amount of paint necessary to cover a given area should be carefully weighed (see Covering Power of Pigments, Chapter XIV.).

Two prepared boards should be painted with each of the paints under test, so that one can be hung outside and tested as to its durability and wearing properties under weathering influences, while the other is kept indoors.

The time the paint takes to dry inside and out is carefully noted, since as a general rule those paints which require a longer time to dry are more durable and wear better on outside exposure than the quick-drying paints. On the other hand the fact should not be lost sight of that if the paint dry too slowly its surface is liable to pick up dust and tend to absorb moisture; further, should by any chance rain fall before the surface has set hard then the paint will be apt to become soapy and streaky, and dry off patchy, or even wash off altogether in places. Under these conditions the durability and protective properties of the paint will be seriously interfered with, and after a few months' exposure the paint surface will probably chalk badly and eventually wash completely off.

The time a paint takes to dry outside depends on the nature and composition of the paint as well as on the temperature of the atmosphere and the general weather conditions prevailing at the time of painting. Cold, damp, foggy weather will naturally tend seriously to retard the drying operation, whereas warm, dry weather will accelerate it.

A paint which takes longer to dry than eighteen hours on outside painting should be speeded up by the addition of paste or liquid driers (see Chapter XX.).

The condition of the dry painted surface after it has set hard should be carefully examined and note taken as to its lustre ("face") smoothness and freedom from coarse particles, its flowing properties and absence of streakiness or brush marks.

The toughness and elasticity of the dry paint film may be tested by scraping it with a sharp knife. If it should show any signs of brittleness, then it may be taken for granted that the paint will wear badly and is only suitable for indoor use.

The painted boards which are exposed outside for weathering tests should be

examined every month and note taken of any signs of deterioration or wear such as blistering, chalking, cracking or shelling off.

A high-class paint should wear well for four or five years, when exposed to weathering influences, without showing any indications of cracking or shelling off. The best class of paints are those that wear down evenly, showing only a moderate chalking effect and leaving a surface which only requires washing down to render it suitable for repainting.

Paints manufactured for particular purposes should obviously be tested out as nearly as possible under the conditions they are to be used in order to ascertain how closely they possess the properties required of them; for example, anti-corrosive paints should be tested out on iron work; priming paints, on both wood and iron, and so on.

PART II

The Inorganic and Organic Pigments. Their Preparation and Properties

CHAPTER VI

THE WHITE PIGMENTS

THE group comprising White Pigments is not a very large one, but it includes amongst its members some of the most important and widely-used pigments at the disposal of the manufacturer of paints and protective coatings. Many of these white pigments, for example white lead and zinc oxide, are more or less familiar to everyone, and are in daily use, although their method of preparation and their properties may not be quite so well known.

For the sake of convenience the white pigment group may be divided into two sections, viz. :—

- (a) The naturally occurring white pigments, and
- (b) The manufactured white pigments, *i.e.* those pigments which are produced by chemical means.

(A) THE NATURALLY OCCURRING WHITE PIGMENTS

In this group are those white pigments which occur in nature in a more or less pure state, and require only a simple process such as grinding and levigation to render them suitable for use. The following well-known and widely distributed natural occurring pigments are comprised within it, viz., barytes, whiting, terra alba, China clay, French chalk, white earth.

These pigments are often classified under the name of “the inert pigments” or “extenders,” as their body and covering power is exceedingly small.

BARYTES (BaSO_4)

(Barium Sulphate, Schwerspat, Permanent White, Sulfate de Baryte.)

Barytes was discovered by Scheele in 1774 in a mineral called terra ponderosa, or ponderous spar. Bergman gave it the name of barytes, from the Greek word “barys” (heavy).

It occurs very widely distributed, as the mineral heavy spar, in various parts of England, Germany, America, Spain, Italy and other countries. Frequently it occurs associated with lead ores such as galena; and in the Derbyshire lead mines the workmen call it "cauk."

The purity of barytes varies considerably according to the locality in which it is found; moreover often in the same mine seams of barytes are obtained some of which are of a pure white colour whereas others are of a yellowish or greyish-red hue, due to the presence of iron.

Sometimes large masses of crystalline barytes, in the form of large rhombic prisms, are met with, but the amorphous or non-crystalline variety is more usual.

Manufacture.—The manufacture or preparation of barytes for use as a pigment or base is very simple. The large masses of crude mined material are sorted out so that the whiter portions are separated from the reddish-yellow and discoloured portions, the latter being made use of in the preparation of the commoner grades of finished barytes. The crude material, after this preliminary grading, is then ground in large flat stone mills under water till the material is perfectly fine.

This grinding process is a very tedious operation, and sometimes—especially in the more crystalline varieties—it is necessary to put the material through the stone mills from four to ten times before it is fine enough for use.

The stones used in the mills must be exceedingly hard, and it has been found by experience that French stones give the best results, on account of their great hardness.

As a rule the mills are arranged in series so that the ground material passes from one mill to the other till the requisite degree of fineness is attained. The ground material, as it comes from the mills, is conveyed into settling tanks, as in the usual process of levigation (see Chapter VII.), so that any coarse particles are separated out and ground over again.

The material thus obtained is known as "water-floated" barytes, and requires to be bleached to make it suitable for the best grades of white barytes.

This bleaching operation is carried out by the addition of a small percentage of sulphuric acid or hydrochloric acid, continual stirring being necessary so as to get complete admixture. Steam may be passed through to accelerate the operation.

By means of this acid treatment all the iron which is present in the barytes is removed and a perfectly white product is produced.

The barytes is next well washed till all the acid is removed, then dried and sieved, when it is ready for use.

In many cases the sorted-out barytes is simply ground in the dry state three or four times through special stone mills till the required degree of fineness is secured. This is usually done in those cases where the barytes mined is of a somewhat soft amorphous character and readily lends itself to this operation.

The ground barytes thus obtained is then subjected to a sifting process by means of compressed air; in this way "air-floated" barytes of an excellent degree of fineness is obtained.

It is usual to add a small trace of ultramarine blue during the grinding operation, whereby the whiteness of the barytes is much improved.

The barytes comes on to the market packed in 1 or 2 cwt. bags, or about 8 cwt. casks, and is comparatively cheap. Owing to its cheapness it forms an ideal "extender" or adulterant for use in conjunction with other pigments, especially white lead on account of its high gravity and low oil consumption.

Barytes is sold under twelve or more different grades, each varying as regards colour and fineness of grinding.

These grades may be roughly divided into three, viz., Best Superfine White Barytes, Seconds Barytes, and Common Barytes.

By far and away the best barytes that comes on to the English market is imported from Germany—this not only on account of its pure white colour, but also because of the excellence of its texture and the fineness of its grinding.

This is due to the fact that in Germany there are very large deposits of naturally occurring soft amorphous heavy spars, and also, to a lesser extent, because owing to the cheap water power the cost of a large number of grindings which would be prohibitive in other countries does not add very materially to the cost of production.

Spanish Barytes is of rather an open texture, and there is often associated with it a certain proportion of sulphate or carbonate of lime.

English Barytes is unfortunately rather coarse in texture and inferior in colour as compared with that of the German.

Properties and Uses.—Barytes or barium sulphate (BaSO_4) is used in enormous quantities in the paint trade as an adulterant or "extender" for mixing with other pigments whereby their cost is considerably reduced. Its value is dependent on the whiteness of its colour and the fineness of its texture or grinding.

It is a heavy white pigment, and owing to its crystalline nature has always a slight gritty feel. It is one of the heaviest white pigments or "extenders" known, and has a specific gravity of 4.48. Its oil absorption is very low, and it only requires about 8.5 per cent. of oil to grind it into a paste form.

Barytes is practically insoluble in water (100 gms. of water at 10°C . dissolve .0002 gms. BaSO_4) and is quite permanent; it is not attacked by either acids or alkalies, and can be ignited without undergoing any change.

As previously stated it is largely employed, because of its low oil absorption, as an adulterant for white lead.

Barytes has practically no covering power or body; hence owing to its lack of strength and transparency it makes an excellent base for aniline colours, these colours not being in any wise affected by it.

The use of barytes in paints cannot be regarded simply in the light of an adulterant, since by its use in, for example, Brunswick greens, the tones of the associated pigments (chrome and blue) are thereby much enhanced, and at the same time a paint is produced of much superior working properties and at considerably less cost.

Analysis of Barytes.—A complete analysis of a barytes is as a rule not required,

as the qualitative tests are quite sufficient to indicate whether the material is up to the required standard.

The chief requirements of a first-class barytes are that it shall be of a good white colour and fine texture.

Colour and Fineness.—The simplest way to test the colour and fineness is to place a portion of the sample on a white palette alongside of the standard and add a few drops of turpentine to each, and note the resultant colour. A creamy white is always to be preferred to a greyish white.

The texture is next examined by grinding the sample moistened with turpentine on the porcelain slab with an iron palette knife. The comparative degree of fineness and texture can at once be recognised after a very little experience.

Samples of barytes containing sulphate or carbonate of lime may be recognised by their somewhat open texture; if silica be present then the barytes feels harsh, and rapidly discolours after a little grinding, owing to the wearing action of the hard silica on the iron palette knife.

A quantitative estimation of the amount of coarse particles in a barytes may be made by putting a weighed quantity through a series of sieves of different degrees of fineness and weighing the residue.

A still more reliable method consists in using an Elutriator (see Fig. 8). The Elutriator proper consists of a short tube of similar diameter to an ordinary burette, *i.e.* such that 1 c.c. of fluid occupies 1 cm. of length. It is open at the top and reduced at the bottom to about 2 mm. bore. This end is curved up in a U form.

Into the upper end fits a perforated rubber cork bearing an inverted U tube. The lower end is connected by means of rubber tube to the lower of two tandem stopcocks A and B. A removable pinchcock fits this rubber tube. The upper stopcock is connected to a water-pressure regulator which, by means of simply raising or lowering with the aid of a cord and pulley, regulates the speed of flow through the Elutriator.

Upon erection, the cock A is fully opened, the regulator raised to the point 50, and the cock B is adjusted till just 50 c.c. of water are discharged from the inverted U per minute. The cock B is never touched afterwards, and any point on the scale corresponds to a flow of that number of c.c. of water per minute through the instrument.

In use the Elutriator is detached, half filled with water, a weighed quantity of the barytes dropped in, the open end corked, and the contents thoroughly shaken. It is then placed in position and the flow of water established for five minutes. It is

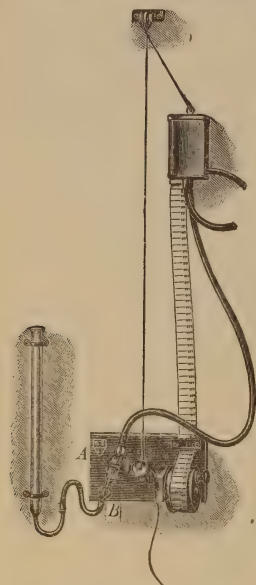


FIG. 8.—ELUTRIATOR.

removed, half emptied by decantation, corked, shaken, and the flow continued for another five minutes.

Similarly a third shaking and washing is given, the contents being finally passed through a weighed filter, dried in the steam oven and weighed, giving the percentage of coarse matter. The rate of flow must be found experimentally to suit each user's requirements and also varied according to the heaviness of the barytes under test.

Free Acid.—As acid is used in the bleaching of barytes it is necessary to make sure that it has all been washed out, and that the barytes is perfectly neutral.

The easiest method of doing this is to place a small portion of the sample in a watch glass, adding a few drops of distilled water, and then introducing a strip of blue litmus paper. Any reddening of the latter will indicate the presence of an acid.

Iron Carbonates, Lime, etc.—Boil a portion of the sample, say 1 gm., with a little hydrochloric acid. Any effervescence indicates carbonate of lime or barium. Filter off, wash well, dry and weigh. This gives the percentage of barium sulphate provided no silica is present.

To the filtrate add (1) barium chloride solution. A white precipitate indicates calcium sulphate.

(2) Three drops of nitric acid and a little potassium ferrocyanide solution. A blue coloration indicates iron.

If carbonates be present then test for calcium and barium in the filtrate in the usual way.

WHITING (CaCO_3)

(Paris White, Spanish White, Chalk, Calcium Carbonate,
English White, Kreide, Craie.)

The vast masses of limestone, chalk and marble which are found in every part of the world are combinations of lime and carbon dioxide, and are represented by the formula CaCO_3 (calcium carbonate).

Chalk is essentially a rock of organic origin, and the microscope shows that it consists largely of the shells of minute organisms. Calcium carbonate is dimorphous, and occurs in nature in two well-defined crystalline forms, viz., in the form of rhombic crystals as aragonite, and in trigonal crystals as calcspar or Iceland spar. Marble is made up of minute crystals of calcite or calcspar.

Iceland spar is a calcium carbonate of a very high degree of purity, and can be obtained in clear crystalline blocks containing 99.9 to 100 per cent. CaCO_3 .

Chalk and limestone are found very abundantly on the English coasts, and in various other parts of the country, in a more or less pure condition, though often it is associated with magnesium carbonate, clay and silica.

Marl is a mixture of limestone and clay.

Manufacture.—The crude quarried chalk is prepared for use as a pigment by grinding under water and levigating to separate the coarser material. The wet

whiting from the settling tanks is dried on a long hearth heated by fires, care being taken not to overheat, otherwise lime may be produced.

The dried whiting is then sieved and bagged ready for use. Whiting is sold in several varieties. The purest and finest is known as Paris white, the second under the name of Gilders whiting is often sold in large lumps or "nubs." The commonest variety of all is of course called simply whiting.

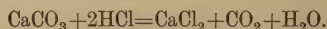
The crudest material from the early settling tanks is put on the market under the name of whiting sand; it is of a coarse texture due to the large amount of silica associated with it.

Properties and Uses.—Paris white or whiting is of a pure white colour and has a soft texture. Its specific gravity is 2.5. It is a bulky pigment, and requires a comparatively large amount of oil to grind into a paste (18 per cent.).

It is quite stable to light and is unaffected by sulphuretted hydrogen. It may be mixed with all pigments without change.

It is practically insoluble in water (100 gms. dissolve .00018 gms.), but is more soluble in water containing carbon dioxide, forming acid carbonate of lime $\text{CaCO}_3 \cdot \text{H}_2\text{CO}_3$. The temporary hardness of water is due to this acid carbonate of lime being dissolved in it and may be removed by boiling.

It is soluble in all dilute acids with effervescence due to the evolution of carbon dioxide, thus :—



On strong ignition the carbonate of lime is decomposed with evolution of carbon dioxide and formation of quicklime :—

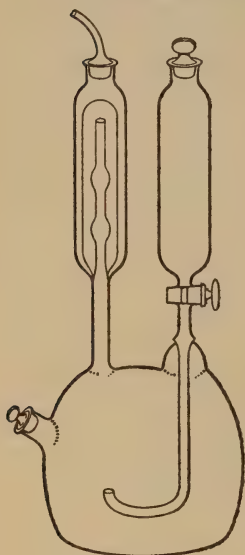
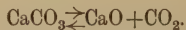


FIG. 9.—SCHRÖTTER CO_2 APPARATUS.

Paris white or whitening has no body or covering power when ground in oil, but has a transparent dirty yellowish appearance. On the other hand, it has splendid covering power in water, and for this reason is used in very large quantities in the manufacture of distempers and kalsomines. It is also largely used when ground into a stiff paste with linseed oil as putty for glaziers' use.

Analysis.—An analysis of whiting is rarely called for, as its value is judged by its colour, and the fineness of its texture and freedom from grit.

If required all that is necessary is to dissolve in hot dilute hydrochloric acid and filter off and weigh the insoluble matter, equals silica (SiO_2).

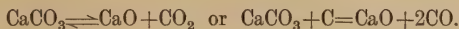
The calcium may be estimated by adding ammonia and precipitating with ammonium oxalate (after the removal of any iron or alumina that may be present) and igniting and weighing as lime (CaO).

The carbon dioxide may be estimated in the Schrötter apparatus (see Fig. 9).

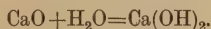
LIME (CaO)

(Quicklime, Calcium Oxide.)

Quicklime or lime is made on the large scale in Buxton and elsewhere by heating limestone in kilns along with coal. The burning of the coal in the presence of the air which is drawn through the kilns produces a white hot heat whereby the calcium carbonate is decomposed, carbon dioxide being evolved and lime left behind.



When water is added to lime combination takes place and a considerable amount of heat is evolved, calcium hydroxide being formed. The lumps of quicklime fall to powder when thus treated, slaked lime being produced; with sufficient water to bring it to a creamy consistency "milk of lime" is produced.



Lime is used, mixed in water, for lime washing. It is also used for making mortars and cements; and in the varnish industry as a hardener for rosin (see Chapter XVIII.). It is likewise employed for many purposes which it is unnecessary to mention here.

TERRA ALBA

(Gypsum, Calcium Sulphate, Light Spar, Gips.)

Gypsum occurs native in large quantities in various parts of the world. It is mined extensively in this country in Derbyshire, Staffordshire, and other localities.

It occurs as the anhydrous sulphate CaSO_4 as anhydrite; and in the hydrated form $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as gypsum, alabaster, selenite, agalite, etc.

The natural deposits of gypsum or lightspar are prepared for use in the pigment industry by a simple process of grinding much in the same way as described under barytes.

Properties and Uses.—Terra alba possesses a good white colour; it has a poor body and is rather transparent, hence has no real covering power. Its specific gravity is 2.3. Its texture is very open or woolly; hence it is not used very much with other pigments except in the case of ultramarine and lead chromes. With lead chromes it replaces whiting as the latter has a tendency to redden the shade of yellow chrome.

Venetian reds contain large quantities of terra alba, but this has been produced by, as a rule, the action of calcium carbonate on the ferrous sulphate during the ignition process in the manufacture of this class of red pigments.

Gypsum contains 2 molecules of water of crystallisation and so has the formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Plaster of Paris.—When gypsum is heated to about 140°C . it is rendered anhydrous, and is converted into plaster of Paris; and when this is made into a paste with water it rapidly hardens, and is used as a cement.

Calcium Sulphate possesses the peculiar property (lime resembles it in this respect) of being somewhat less soluble in hot water than cold, requiring over 500 times its weight of water at 100° C., but only 400 times at 35° C. to dissolve it. Calcium sulphate will dissolve when boiled for a long time with excess of hydrochloric acid.

It is largely used by paper stainers, and for "weighting" cotton goods; also in distempers.

CHINA CLAY

(Kaolin, Pipe Clay.)

China clay or kaolin is widely distributed in England, France, Germany, and other places. Some of the finest China clay for use in the manufacture of pottery is obtained from Cornwall.

When potash felspar (K_2O , Al_2O_3 , $6SiO_2$) and many other natural aluminosilicates are exposed to weathering influences they are in process of time converted into an insoluble white crystalline or amorphous (colloidal) powder, such as China clay. Hence the deposits of China clay may be said to be due to the weathering of the aluminosilicates.

Granitic rocks with felspar as a matrix disintegrate in process of time, leaving the clay behind mixed with the more resistant varieties of mica, quartz, and other minerals, which originally formed the granitic rock.

Manufacture.—China clay is obtained in a more or less pure state, that is free from the unweathered quartz, mica, etc., by a simple process of washing and settling or levigation. The settling tanks are so arranged that all the lighter mica, which comes over after the heavier quartz has settled out, is caught in a series of large troughs, thus allowing the material that finally passes over into the last settling tanks to be practically pure China clay; this is dug out of the settling pits and dried.

Properties and Uses.—China clay is essentially an hydrated silicate of alumina, which has very nearly the empirical composition— $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.

It is a white powder with an extremely soft and fine texture. Its specific gravity is about 2.2. It is a very bulky material, hence requires a lot of linseed oil to grind it into a paste form. Being transparent in oil, it lacks body and covering power. It is used extensively in paints as a suspender for preventing settling and is very useful in dipping paints (see Chapter III.), for on account of its low specific gravity it keeps the pigments associated with it in suspension. In addition, China clay is largely used as an inert base on which to strike or precipitate aniline dye-stuffs. It is quite permanent and stable to light, and is not affected readily either by acids or alkalies.

In the manufacture of ultramarine blue it plays an important part (Chapter VIII.).

MAGNESIUM SILICATE

(Talc, Steatite, French Chalk.)

Magnesium silicate occurs in nature as olivine Mg_2SiO_4 ; serpentine $\text{Mg}_3\text{Si}_2\text{O}_7 + 2\text{H}_2\text{O}$; talc, soapstone or steatite $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. Asbestine, asbestine pulp, asbestos, and meerschaum are double silicates of calcium and magnesium.

Talc or French chalk has a soft unctuous feel, and on account of its low specific gravity is much used in paints to prevent settling. It is very inert and has properties similar to those of China clay. It is easily recognised under the microscope by the fibrous structure of its particles.

Silica (Silex).—Silica (SiO_2) is one of the most important compounds forming the crust of the earth. In a crystalline condition it occurs as quartz or rock crystal and tridymite. In an amorphous form it is met with in enormous quantities in the deposits known as kieselguhr. This substance consists of the remains of extinct diatomaceæ and is come across in various parts of Germany and America.

Diatomaceous earth, also called tripoli, kieselguhr, Fuller's earth, or infusorial earth, is largely used as a bleaching agent for oils; in the manufacture of dynamite, cement, and for many other purposes.

Silica obtained by crushing quartz very finely and sieving through 120-200 mesh sieves comes on to the market as a harsh-feeling, coarse-grained white powder. In the paint trade it is largely employed, ground in oil and varnish, as a wood filler or priming paint for wood for filling up the grain before staining and varnishing.

STRONTIUM SULPHATE

(Strontium White.)

This material occurs naturally as the mineral celestine (SrSO_4). It is sometimes used as a substitute for barytes, but is not so satisfactory, as owing to its higher specific gravity it absorbs more oil.

Its properties are very similar to those of barytes, from which it may, however, be readily distinguished by the bright crimson colour which it gives in the Bunsen flame as compared with the well-known green barium flame which is characteristic of barytes.

Barium Carbonate (BaCO_3).—This substance is found in Germany, England, and America native as witherite. It is practically never used as a pigment in this country, though a certain quantity is used in America as an extender for readily mixed paints.

White Earth.—This material is similar in composition to the native augites described under Green Earth (see Chapter IX.), and is a magnesium aluminium silicate. It is of a transparent white colour, and like green earth has the property of fixing basic dye-stuffs. In fact, with dye-stuffs such as methyl violet and methylene blue, where it is essential that the clearness of the tones should be retained, it is used in preference to green earth.

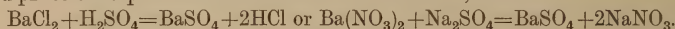
(B) THE WHITE INORGANIC CHEMICAL COLOURS

Under the classification of White Inorganic Chemical Colours are white pigments which are produced by chemical means, as distinguished from those naturally occurring white pigments which have already been described.

BLANC-FIXE

(Permanent White, Precipitated Barium Sulphate.)

Blanc-fixe, or, as it is sometimes called, artificial barytes, has the same composition as the naturally occurring barytes or heavy spar, BaSO_4 ; in fact, it is precipitated barytes. It is produced as a fine white precipitate whenever a solution of a sulphate or sulphuric acid is added to a barium salt, thus:—



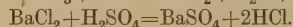
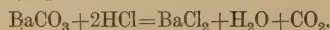
It is marketed either as a fine white powder or as a paste or pulp containing about 20 per cent. water.

Manufacture.—The raw materials that are used in the manufacturing scale for the production of blanc-fixe are either natural barytes or witherite (BaCO_3). The cheapest and at the same time the most convenient process (and which is in general use), is to take the mineral witherite as the starting point.

The witherite is ground to a fine powder and decomposed in tanks by means of hot dilute hydrochloric acid, whereby great effervescence takes place owing to the liberation of carbon dioxide. The barium chloride solution thus formed is allowed to settle, and is then run through filters into precipitating vats. Sulphuric acid is added till all the barium present is thrown down as barium sulphate. Glaubers salts (sulphate of soda) or other cheap sulphates may be used in place of sulphuric acid to precipitate the barium sulphate.

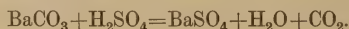
The precipitate of the blanc-fixe thus formed is well washed till quite neutral and free from all soluble matter. It is then filter pressed, and sold in the form of a paste containing about 20 per cent. of water; or if required in powder form it is dried in vacuum stoves.

The course of the reactions that take place during this operation may be expressed by the following equations:—



The ground witherite can also be treated directly with hot dilute sulphuric acid, though in this case the blanc-fixe thus produced requires careful sieving to remove all the impurities that may be present in the raw material.

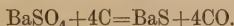
The reaction proceeds as follows:—



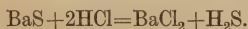
As the decomposition of the witherite by treatment with the hot dilute acids is always accompanied by great effervescence due to the liberation of large quantities of carbon dioxide, so care must be taken to provide plenty of ventilation.

The manufacture of blanc-fixe from natural barytes or heavy spar is carried out as follows :—

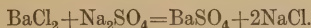
The finely ground natural barytes is calcined with coal or charcoal in a reverberatory furnace at a red heat, barium sulphide being thereby produced as under :—



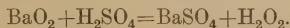
The barium sulphide is then digested with hot dilute hydrochloric acid, sulphuretted hydrogen is evolved and barium chloride remains in solution :—



The solution thus produced is allowed to settle, then filtered to remove all solid impurities. Sulphuric acid, or sulphate of soda or magnesium solutions, are next run in causing barium sulphate to be precipitated. This is washed and dried as before.



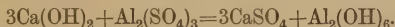
Considerable quantities of blanc fixe are also obtained as a by-product in the manufacture of hydrogen peroxide from barium peroxide, thus :—



Properties and Uses.—Blanc fixe is a white powder possessing an extremely fine and soft texture. It is quite permanent, and as it is simply a precipitated barium sulphate its general properties—with the exception of its fine texture—are similar to those of barytes and need not be further described. It is largely used as an inert base for coal tar dye-stuffs (see Lakes, Chapter XIII.), and also as a filler or extender for enamel paints where a fine extender material is essential.

Its specific gravity is 4.3. On account of its bulkiness it requires more oil than barytes to convert into paste form ; and by reason of its lightness and non-settling properties it is largely used in dipping and spraying paints. Owing to its amorphous character it has more covering power than barytes ; its cost, however, is about twice as great.

Satin White.—This product is a mixture of alumina and calcium sulphate. It is prepared by mixing the equivalent proportions of freshly slaked lime—mixed with water to form a cream—and sulphate of alumina or alum solutions. The reaction may be expressed by the following equation :—



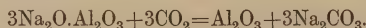
The precipitate of satin white thus formed is well washed and may be filtered and dried, but is more usually sold in the pulp form. Satin white is a white pigment with moderate covering power. Its chief use is in the paper trades.

ALUMINA (Al_2O_3) and ALUMINIUM HYDROXIDE ($\text{Al}_2(\text{OH})_6$)

(Tonerdehydrat.)

Alumina occurs in nature in the crystalline form as emery and corundum. Aluminium hydroxide is precipitated from solutions of alum or sulphate of alumina by caustic alkalis (soluble in excess) ; ammonia or ammonium carbonate.

It is also precipitated from alkaline aluminates by carbon dioxide, which is the method in use for the manufacture of the material on the large scale. The reaction may be expressed thus :—



The hydroxide which is prepared by the addition of ammonia or ammonium carbonate, or caustic alkalies, is a bulky, flocculent, gelatinous precipitate possessing the property of acting as a mordant in carrying down dye-stuffs in solution and absorbing them. On this account it is largely used in the manufacture of Lakes (see Chapter XIII.). The production of the hydroxide of alumina may be represented by the following equation :—



The freshly precipitated alumina hydroxide (often called alumina) is readily soluble in excess of caustic alkalies such as caustic soda, and in dilute acids.

By igniting the hydroxide the whole of the water is driven off and the anhydrous oxide Al_2O_3 is obtained as a pulverent white powder.

Aluminium hydroxide is largely used as a base by the lake manufacturer owing to its mordant properties. It is rather transparent, hence the lakes formed with it are deficient in body but possess bright clean tones and strong staining properties. The lake manufacturer produces his "alumina" base in the following way: Alum, or 18 per cent. sulphate of alumina (iron free quality), is dissolved in about twenty times its weight of hot water. Then a dilute solution of soda crystals, soda ash, or ammonium carbonate is run in, with continual stirring, till all the alumina is precipitated. The precipitate is well washed by decantation with cold water till perfectly neutral and free from all soluble matter.

It is then ready to be used as a base for fixing on the various dyestuffs—either natural or artificial—which it is desired to precipitate.

The following example will give a clear idea of how this process is carried out.

Process 1. Alumina Hydrate Base.—200 lbs. of sulphate of alumina are dissolved in 500 gallons of hot water (110° F.). Stir in slowly 90 lbs. of soda ash (or its equivalent of soda crystals or ammonium carbonate) dissolved in 90 gallons of cold water. Wash well till free.

The above proportions should give about 50 lbs. of dry alumina hydrate.

The precipitate is used in the pulp form. If it should be required in the dry state, care must be taken to dry at a very low temperature otherwise a tough, horny mass of alumina will be produced, which will be quite unsuitable as a base.

As mentioned above the base thus produced is of a very transparent nature, and on account of this the lake manufacturer very often makes an addition of blanc-fixé (precipitated barytes) so as to give more body to it. This is especially the case where the lake is going to be used as a body colour.

The following process for the manufacture of an alumina blanc-fixé base will illustrate the methods in vogue for the preparation of this base.

Process 2. Alumina Blanc-fixe Base.

Mix 200 lbs. sulphate of alumina, and

90 „ soda ash (as in process 1). Stir into this

210 „ barium chloride dissolved in 100 gals. water.

Wash till free. This gives about 250 lbs. of dry alumina blanc-fixé base.

WHITE LEAD

(Flake White, Kremnitz White, Bleiweiss, Ceruse, Blanc de Plomb, Blanc d'Argent.)

White lead is a basic lead carbonate represented by the formula $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$. It was known to the ancients; Theophrastus, Pliny, and Vitruvius describe its method of preparation from metallic lead and vinegar.

At the present time white lead is probably the most important white pigment that is manufactured by chemical means, and the yearly output of this material is enormous.

There are a large number of factories in England, Germany, and America engaged in the manufacture of this pigment, and the processes in operation for the conversion of blue lead into white lead are very varied.

Owing to its poisonous nature special regulations and legislation have been introduced from time to time to minimise the risks attendant on the manufacture and use of this pigment. In fact, in some countries, *e.g.* France, its use has been prohibited and its place taken by zinc oxide; in this country it has been proposed that its use should be abandoned.

The question of the use of white lead was investigated by two Committees appointed by the Home Secretary in 1911. Their reports, issued in 1915 and 1920, were unfavourable to its continued use; and in the belief that adequate substitutes were available, they recommended that the use of white lead for paint material should be prohibited. No effect was, however, given to this recommendation.

Overwhelming evidence of the failure of many of these substitutes led to the appointment by the Home Secretary in 1921 of a new Committee, with Sir Henry Norman as Chairman. This Committee was unable to support the recommendations of its predecessors, and was of opinion that for outside painting and for certain kinds of internal painting "there is at present no efficient substitute for white lead."

This is also the view of Professor H. E. Armstrong and C. A. Klein, who have studied the subject exhaustively.

The League of Nations at Geneva has also carefully considered the whole of the facts brought before its notice in regard to the injurious and poisonous nature of this pigment. The subject is a highly controversial one and outside the scope of this book.

Many substitutes for white lead have been offered at different times under such names as non-poisonous white lead, such as sulphate of lead, and others; but these have all been found to be lacking in those essential properties of density and body which are characteristic of all well-made white leads.

Other non-poisonous white pigments, notably zinc oxide, lithopone, antimony white, and recently titanium white, have been proposed as alternatives to white lead; and, at the present time, enormous quantities of zinc oxide and lithopone are consumed yearly in the manufacture of white paints, for both inside and outside work.

It cannot be denied that as regards density, body and obscuring power, white lead is pre-eminent (though sometimes it is claimed that titanium white is its equal; its price, however, is twice as high. See Titanium White, page 56). Moreover, as a priming coat for protective work on outside structures it is unsurpassed; in fact, the durability and hard-wearing properties of white lead are altogether remarkable.

Perhaps it is only fair to add that manufacturers of white lead assert that as a result of the stringent regulations that are now in force as regards ventilation, dust, and cleanliness, cases of lead poisoning are practically non-existent in the works engaged in the production of this pigment. Further, that if users were equally careful to carry out faithfully the rules laid down for them, lead poisoning would be a negligible risk.

The manufacture of white lead on the large scale is very old; and for various reasons it is supposed that the first works to be erected for its production on a commercial scale were situated in Holland. The "Dutch process," as it is called, has been carried on for many hundreds of years in Holland; and even up to the present time the old Dutch or stack process is in use in this and other countries and the white lead thus produced is still the most highly esteemed on account of its unsurpassed density and body.

The Manufacture of White Lead.—White lead or basic carbonate of lead ($2\text{PbCO}_3\text{Pb(OH)}_2$) is manufactured by a great many processes. Innumerable patents have been taken out at different times for the production of this pigment, and it would be quite impossible within the space at our disposal to describe, or even mention, a tenth of them. The reader who is particularly interested in the subject is referred to the special treatises and patent specifications dealing with it (see Bibliography).

We will now describe the Dutch process, or Stack process, as it is more commonly called, for the manufacture of white lead.

1. *The Dutch Process ("Stack" White Lead Process).*—This process, as stated above, has been carried on in Holland for many hundreds of years—it was said to have been "old" in 1662—with little change as regards the main essentials. From Holland it spread to other countries till it is now employed in all parts of the world.

Shortly, it depends on the action of acetic acid upon metallic lead in the presence of moist air and carbon dioxide.

The molten metallic lead, after the removal of the scum on the top, is cast into rough gratings, or else into thin strips which are rolled up spirally, care being taken to see that the strips of lead are thin and uniform, so that the maximum efficiency in corrosion will take place.

The metallic lead used by the white lead manufacturer should be as pure as possible, as even a small trace of such foreign metals as silver, copper, bismuth, cadmium, antimony, and iron would cause a discoloration of the finished product.

The corroding pots used in the Dutch process are made of earthenware glazed inside, and are provided with shoulders on which the strips of lead or gratings are supported (see Fig. 10), so that they do not come in direct contact with the acid. A layer of 3 per cent. acetic acid (in the old Dutch process vinegar) is first placed in the pot.

The pots vary in size, but as a rule average about 8 inches high by 4 inches in diameter. They are placed upon a thick bed of spent tan bark from the leather tanning yards (in the original process dung was used, but owing to the evolution of sulphuretted hydrogen, which discoloured the lead, it was replaced by various substitutes) upon the floor of a shed and covered with planks.

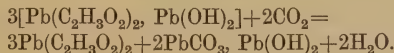
Upon these planks another layer of tan bark is spread, and a second row of pots similarly charged. In this manner the layers of pots are built up to the roof of the shed. The whole is then allowed to remain for about twelve weeks. At the end of this time most of the lead will have been transformed into compact masses of white lead.

Such stacks are very large, say 15 feet square by 20 feet high, and contain many tons of lead; and about 70 gallons of dilute acetic acid to the ton of metal.

The heat developed by the fermenting tan volatilises the acetic acid, which results in the formation of a basic lead acetate thus:—



The basic acetate so formed is decomposed by the carbon dioxide evolved during the fermentation of the tan bark with the production of a mixture of normal lead acetate, and basic lead carbonate thus:—



The lead acetate in the presence of air and moisture reacts upon a further portion of the lead, forming more of the basic acetate of lead, which is once more decomposed by carbon dioxide:—

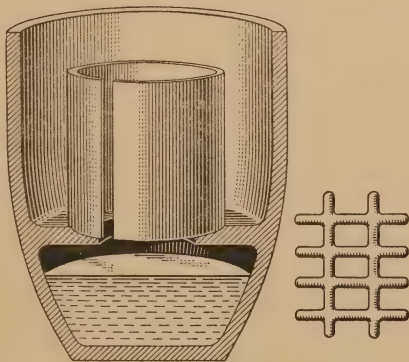
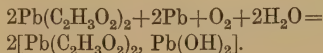


FIG. 10.—WHITE LEAD CORRODING POT.

In this cycle of reactions, therefore, the acetic acid acts as a carrier, a comparatively small quantity being able to convert theoretically an indefinite amount of lead into white lead.

At the end of the period allowed for the complete conversion of the metallic lead into white lead the stacks are unloaded, great care being taken to ensure that none of the spent tan falls into the pots.

On opening the pots it will be found, if the operation has been carried out properly, that practically all the acetic acid has disappeared and that the strips of lead are nearly all corroded away, leaving a thick deposit of white lead. The pots are emptied out, and the contents thoroughly ground through rollers and sieved so as to remove all the metallic lead that may be present. The separated blue lead is remelted to be used over again. The white lead is thoroughly washed to remove all the lead acetate, ground, filter pressed, dried and sifted. The first wash liquors containing the sugar of lead are treated so as to recover this material.

The main objections to the Dutch or Stack process are (1) the great length of time required for the conversion of the blue lead into white lead, and (2) the fact that the white lead thus produced, although unsurpassed for opacity, density, and body, is yet somewhat lacking as regards the purity and whiteness of its colour. For these reasons, among others, many attempts have been made to speed up the process, and at the same time produce a white lead of a better colour. The most important of these processes is what is known as the chamber process.

The Chamber Process or the German Process.—The chamber process for the manufacture of white lead was first introduced in Germany about the year 1750. The earliest processes were simply a modified or improved form of the Dutch process, and were carried out as follows :—

The strips of metallic lead were suspended in wooden boxes, on the floor of which were placed a mass of fermenting grape husks, and other vegetable material, whereby acetic acid and carbonic acid were generated. The boxes were put in a warm room, and the temperature kept at about 50° C.

The heat generated in the Dutch process, as described above, was generated by the natural fermentation of the tan barks, whereas in the chamber process artificial heat is used by means of which the fermentation is accelerated at will, while the acetic acid vapours along with the moisture and carbon dioxide which are evolved, corrode the lead, converting it into white lead.

Later improvements consisted in partly replacing the fermentation materials by vinegar, which was simply poured into the box.

In the modern chamber process the vinegar, or weak acetic acid, and the carbonic acid are both prepared outside the chambers and passed in along with steam. Further, the lead is "feathered" or rolled into very thin long strips and hung up on wooden racks in a large brick chamber.

These chambers when full hold from five to ten tons or more of metallic lead, and the racks holding the strips of lead are so arranged as not to interfere with the efficient circulation of the gases and steam.

When the chamber has been fully charged, all the doors and windows are closed, and the acetic acid is supplied to the chambers in the form of vapour by boiling weak acetic acid (generally wood vinegar) in copper pans.

The acetic acid vapour and steam, accompanied by air, are passed through the chambers for two or three days whereby the basic acetate of lead is formed.

On the completion of this stage, carbon dioxide, obtained by burning charcoal or coke, is introduced in a steady stream together with more acetic acid vapours whereby the acetate of lead is converted into white lead. At the end of about four weeks the process is finished. The chambers are emptied, and the white lead recovered in the same way as described under the Dutch process.

The Chamber process for the manufacture of white lead is not quite so simple as would appear from the above description, and very great care must be taken at all stages of the process if a good coloured and dense opaque white lead is to be obtained.

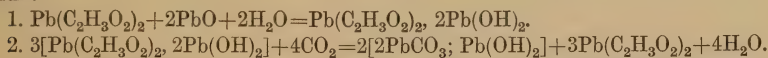
Too much carbon dioxide, if introduced at too early a stage, will tend to produce an extensive amount of carbonate of lead, which would cause loss of opacity and density. The amount of air, moisture or steam, and acetic acid introduced all require to be regulated to a nicety to secure the best results. Hence long experience and very careful supervision are necessary to the successful carrying out of this process.

The white lead obtained by the chamber process is superior in colour to that of the Dutch process, but does not equal it as regards density and opacity.

The chamber process, with various modifications, is now very extensively worked in this country, Germany, and the United States; and by far the greater part of the lead that comes on to the market at the present time is made by this method.

The French or Clichy Process.—Thenard in 1801 showed that when carbon dioxide is passed through a solution of basic lead acetate white lead is precipitated, whilst acetate of lead remains in solution. Moreover, if this lead acetate is boiled up with litharge a portion of this body is taken up whereby basic lead acetate is again reformed. A process based on this reaction was employed by M. Roard about 1835 in a large factory near Paris, and the product thus obtained was sold under the name of Clichy White Lead.

The reaction that takes place in the French or Clichy process may be expressed thus :—



The plant used in this process is comparatively simple, the method of working being carried out as follows :—

A solution of basic lead acetate is made in this manner, viz. : A solution of neutral acetate of lead (sugar of lead) is boiled in a large wooden vat, provided with a steam pipe, with litharge till it is all taken up and the basic acetate of lead formed.

It is, however, more usual to make the sugar of lead in the white lead works

itself by the action of acetic acid upon metallic granulated lead, or still more quickly by dissolving litharge in dilute acetic acid.

The hot solution of basic sugar of lead of the required density is clarified before use to remove any extraneous impurities, and then run into a large wooden precipitating vat into which dip a large number of pipes, all of which are connected to a large main pipe through which the carbon dioxide is passed.

The carbon dioxide may be obtained by burning charcoal or coke, or liquid carbon dioxide contained in large steel cylinders may be used.

The carbon dioxide is passed into the basic sugar of lead under slight pressure till all the basic carbonate has been precipitated and the top liquor is slightly acid. This takes about sixteen hours. At the end of this period the white lead is allowed to settle out and the supernatant clear liquid is pumped off and returned to the first vat, where it is again boiled up with more litharge to convert it into the basic acetate to be used over again. In this way the process is a continuous one, the same amount of sugar of lead being used over and over again; in practice, however, there is always a certain loss and the liquors require making up from time to time.

The white lead precipitate thus obtained is well washed, filtered, pressed and dried.

The product obtained by this process is of a very nice white colour, but is not equal in body or opacity to that of either the Stack or Chamber process. It is also liable to vary considerably, so that the product is not quite uniform.

There are many modifications of the French process in operation for producing white lead from solutions of lead salts by the action of carbon dioxide, but as they are all based on the process detailed above it is unnecessary to describe them.

Kremnitz White Lead Process.—This process was originally carried on at Kremnitz in Hungary, and the white lead produced by it is considered to be the whitest, and, at the same time, densest or most opaque that is made. It is usually imported from the Continent in 56 lb. boxes, the white lead being cut up into squares or cakes and packed separately in paper.

It is of an extremely dazzling whiteness, and often smells strongly of acetic acid. It is mainly used by artists under the name of flake white or Kremnitz white.

The process is carried out as follows :—

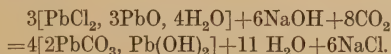
A wooden chamber is fitted with a large number of shelves on which are placed trays containing litharge moistened with vinegar or dilute acetic acid. Carbon dioxide is passed in together with a little air and steam so as to keep the temperature at about 60° C. The paste is raked over from time to time in order to expose fresh surfaces to the action of the carbon dioxide.

After a few weeks the whole of the lead is converted into white lead, which is ground and dried ready for use.

Milner's Process.—This process consists in grinding together litharge, sodium chloride and water, whereby a mixture of an oxychloride of lead and sodium hydroxide is formed :—



Carbon dioxide is then passed into the mixture, which converts it into white lead and sodium chloride thus :—



Montgomery of St Louis has patented a process by means of which molten metallic lead is atomised by a jet of air, and passed into a closed chamber where it comes in contact with a spray of water. The resulting mixture is then carbonated in special cylinders and finely ground.

Many other processes have been worked from time to time for the manufacture of white lead, such for instance as the various electrolytic processes, and those based on the action of alkaline carbonates on sulphates and acetates of lead. But as these have not come into general use there is not any necessity to describe them.

Properties and Uses.—White lead is a basic carbonate of lead of the formula $2\text{PbCO}_3, \text{Pb}(\text{OH})_2$. It is a heavy white amorphous powder with a specific gravity of about 6.45.

It is quite insoluble in water, but is readily dissolved by even dilute acids with violent effervescence due to the liberation of carbon dioxide. It is also soluble in hot alkalis such as caustic soda. On strongly igniting white lead it blackens; the carbon dioxide is driven off leaving a residue of lead oxide.

White lead becomes brown, grey, or black when exposed to the action of sulphuretted hydrogen, ammonium sulphide, or any metallic sulphide soluble in water. The discoloration is due to the formation of lead sulphide; and if treated with a solution of hydrogen peroxide the colour can be restored again.

The composition of white lead varies considerably according to the process by which it is made, and even white lead made by the same process shows slight variations.

The percentage of carbon dioxide varies between 11 per cent. and 16 per cent. and the percentage of lead oxide between 83.75 and 86.75 per cent.

The carbon dioxide in a well made white lead, as a rule, is round about 11.5 per cent.; and in those cases where it reaches 15 or 16 per cent. it is found that the white lead is deficient as regards body and opacity owing to excess of lead carbonate (PbCO_3).

White lead requires about 8 per cent. of linseed oil to grind it into paste form. It is marketed either in powder form or as a stiff paste ground in oil.

On account of its valuable qualities as regards body, opacity, obscuring power, and because of its ease of working under the brush, it is used in enormous quantities as a paint for the protection of outside structures from the weathering influences of the atmosphere.

The composition of white lead should be in the proportion of two parts of lead carbonate to one part of lead hydrate ($\text{PbOH})_2$. The lead hydrate molecule has the property of tending to partially saponify the linseed oil in which the white lead is ground; and owing to this formation of a lead soap (lead linoleate) can be

ascribed the valuable elastic, durable, hard, and non-porous film given by lead white paints.

White lead acts as a drier on the oil in which it is ground; hence paints containing white lead dry very hard and quickly.

It is customary to add a trace of Prussian blue in the grinding of white lead in order to improve the colour; this is especially necessary in the case of the stack white leads, which are, as already mentioned, not such a good colour as those produced by the Chamber or French processes.

Ground white lead is sold as genuine and also in three reduced qualities, viz. Nos. 1, 2, and 3, containing as a rule 25, 50, and 75 per cent. respectively of finest white barytes as an extender to reduce their price.

The two main objections to the use of white lead, as we have already mentioned, are (1) the tendency for white lead paints to turn yellow and finally darken owing to the action of sulphur gases; and also to a lesser extent to the deposition of soot and black particles present in the air, especially noticeable in the neighbourhood of large towns; and (2) its poisonous action producing what is known as lead colic.

SCHEME FOR THE ANALYSIS OF WHITE LEAD

1. *Moisture*.—Weigh 5 gms. on a watch glass, place in an air oven, and keep at 105° C. till constant in weight.

2. *Carbon Dioxide*.—Weigh out 2 gms. in a Schrötter apparatus (Fig. 9, p. 32), and treat with dilute nitric acid. Loss in weight equals CO_2 . Calculate to lead carbonate (PbCO_3).

3. *Total Lead*.—Take 1 gm. and boil in a covered beaker with 50 cc. of dilute hydrochloric acid till all is dissolved. Add 100 cc. of hot distilled water; filter if necessary and wash repeatedly with boiling water. Weigh any residue=Barytes (confirm by flame test).

Evaporate to small bulk; add a little sulphuric acid and continue to evaporate till clouds of sulphur trioxide are evolved. Cool; add a little water and some alcohol. Leave for two hours, then filter through a Gooch crucible. Dry and weigh. Calculate lead sulphate to white lead, or to lead oxide. Subtract total lead oxide in the lead carbonate formed and calculate the difference to lead hydrate.

4. *Calcium*.—This is rarely present, but if so, it may be estimated by precipitating with ammonia and ammonium oxalate.

SPECIFICATION FOR WHITE LEAD

1. The white lead must be a pure basic carbonate of lead, of a good colour and soft in texture.

2. It should contain between 25 and 33 per cent. of lead hydroxide $\text{Pb}(\text{OH})_2$.

3. It should contain not more than 0.5 per cent. of moisture, or matter soluble in water.

4. On reducing with ultramarine blue in the proportion of 10 parts of white

lead to 1 part blue, the resultant shade should be approximately equal to that given by the standard genuine white lead similarly treated.

5. It should be wholly soluble in nitric acid, and the carbon dioxide evolved should be not less than 11 or more than 12·5 per cent.

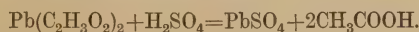
RESULTS OF ANALYSES OF VARIOUS WHITE LEADS

<i>Theoretical Composition.</i>		<i>Stack.</i>	<i>Chamber.</i>	<i>American.</i>
	per cent.	per cent.	per cent.	per cent.
Lead carbonate . .	68·95
Lead hydroxide . .	31·05
	<hr/>
	100·00
<hr/>				
or				
Lead oxide	86·32	86·50	86·25	85·05
Carbon dioxide . .	11·36	11·25	11·50	12·25
Water	2·32	2·25	2·25	2·70
	<hr/>	<hr/>	<hr/>	<hr/>
	100·00	100·00	100·00	100·00

LEAD SULPHATE (PbSO₄)

(Non-poisonous White Lead, Bleisulfat.)

Lead sulphate is obtained by adding sulphuric acid to a dilute solution of acetate of lead. The reaction may be expressed thus :—



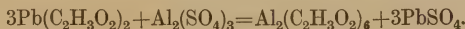
The sugar of lead solution is prepared by the action of acetic acid and steam on granulated lead. The hot acetic acid liquors are continuously pumped on to large tubs filled with the granulated lead till it is all corroded away. To the solution of sugar of lead thus obtained sulphuric acid is added to precipitate out nearly all the lead that is present.

The precipitated lead sulphate is well washed till neutral, then filter pressed and dried. It is often sold in the pulp form containing 20 per cent. of moisture.

The acetic acid liberated may be used over again.

A considerable amount of sulphate of lead comes on to the market in a pulp form known as “lead bottoms.” This is obtained as a by-product in the production of aluminium acetate from alum or sulphate of alumina and lead acetate, a mordant which is used in Turkey Red dyeing.

The formation of the lead sulphate in this process may be expressed thus :—



Properties and Uses.—Lead sulphate is whiter than white lead, but is very deficient in body and covering power; hence it is no use by itself as a pigment.

It is largely used for mixing with lead chromes for making what is known as "genuine" lead chromes.

It is not so heavy as white lead, and consequently requires more oil to grind it into paste form. Its specific gravity is 6.08.

It is insoluble in water, and only with difficulty soluble in acids. Owing to its non-poisonous nature it is often offered by itself or in conjunction with other pigments as "non-poisonous white lead" (Freeman's White Lead).

Sublimed White Lead. Sublimed Blue Lead.—The sublimed leads are manufactured in America by various processes and are sold in many different grades. The average composition is as follows:—

	<i>Sublimed White Lead.</i>	<i>Sublimed Blue Lead.</i>
Lead sulphate . . .	75	48
Lead oxide . . .	20	30
Zinc oxide . . .	5	3
Lead sulphite	8
Lead sulphide	11
	<hr/> 100	<hr/> 100

In addition to these there have also been introduced in recent years in the English and American markets considerable quantities of what are known as "leaded zinc oxides." These products are exclusively manufactured in America, and important claims are made for these pigments in connection with their durable wearing and non-chalking properties. Their composition also varies, but the following analyses of three of these products will indicate their general nature.

	(1)	(2)	(3)
Lead sulphate	20	40	34.0
Zinc oxide	80	60	65.5
Moisture	0.5
	<hr/> 100	<hr/> 100	<hr/> 100

The sublimed leads are manufactured in America from a mixed ore consisting of galena (PbS) and zinc blende (ZnS). These ores are roasted in special furnaces in the presence of a hot blast of air whereby the zinc and lead sulphides are oxidised to lead sulphate, lead oxide and zinc oxide, which pass over as a fume or smoke into large brick chambers where it is collected.

ZINC OXIDE

(Zinc White, Chinese White, Zinkweiss, Blanc de Zinc, Blanc de Neige.)

Zinc white or zinc oxide has the composition represented by the formula ZnO . It is manufactured in enormous quantities, for use as a pigment, in England, Holland, France, Germany, the United States, and Belgium.

There are two processes in operation for the manufacture of this valuable pigment. First, the direct process from metallic zinc, and second, the indirect process in which zinc ores are used.

The introduction of zinc oxide as a pigment to replace white lead was due to Courtois of Dijon, who in 1781 began the manufacture of zinc white. In a report made to the Institut de France in 1808 by Fourcroy, Bertholet and Vauquelin the use of zinc white, manufactured by Mollerat, is recommended as a substitute for white lead on account of its non-poisonous qualities, superior covering power, and its permanency and non-darkening properties.

Leclaire about 1845 established a works at Courcelles on the Seine for the manufacture of zinc white on a considerable scale. He also prepared a drying oil by boiling linseed oil with manganese dioxide for use with his pigment, and thus opened up the way for the general use of zinc oxide as a pigment in place of white lead.

MANUFACTURE

1. *The Direct Process*

The manufacture of zinc oxide by the direct process is carried out on the large scale in the following way :—

Pure metallic zinc, obtained either by calcination of the ores or by electrolytic processes, is introduced into a number of retorts. These retorts are made either of cast-iron or of fire-clay, and are closed at one end, the other end opening out into a main flue which is connected with the condensation chambers. The retorts are built into a reverberatory furnace—as a rule about twenty retorts are used—arranged either in two rows one above the other or else back to back.

After the retorts have been charged with the metallic zinc, and the covers luted on, they are brought to a white heat, causing the metallic zinc to be converted into volatile fumes. These fumes issuing out into the flue come into contact with a current of hot air and thereby ignite, giving off great clouds of white zinc oxide vapour, which is driven over into the collecting or condensation chambers. The zinc oxide is collected from time to time and packed into bags or casks ready for use.

2. *The Indirect Process*

This process is supposed to give a zinc oxide of greater denseness and opacity than that obtained by the direct process ; but owing to the impurities, such as cadmium, present in the natural zinc ores, special care is required in carrying it out, otherwise the colour of the zinc oxide produced would be seriously impaired.

In this process, which is largely used in Holland, the zinc oxide is manufactured directly from the natural occurring zinc ores.

The zinc ores, such as zinc blende (ZnS) and calamine (ZnCO_3) are mixed with coal or coke and heated to a white heat either in earthenware retorts or else in the bed of a reverberatory furnace. The issuing fumes are ignited in the presence of a current of air whereby the metallic zinc burns to zinc oxide, and this white smoke of zinc white thus formed is driven over to the collecting chambers.

In this process the zinc oxide that collects in the chambers nearest the furnace is of a greyish, coarse shade, due to the deposition of metallic zinc, dust, soot and other impurities, whilst the finest snow-white grades collect in the end chambers.

The presence of cadmium in the zinc ores is deleterious to the colour of the zinc oxide formed, tending to give it a brownish hue; hence care must be taken to eliminate it.

Properties and Uses.—Zinc oxide is a soft white tasteless and odourless powder. It is rather bulky, and requires about 18 per cent. of linseed oil to grind it into a paste. Its specific gravity is 5.6.

It is quite insoluble in water, but readily soluble in dilute acids, also in alkaline solutions.

It is quite permanent, and does not darken on exposure to sulphuretted hydrogen fumes; it can be mixed with other pigments without change. On gently heating it turns yellow, but regains its colour on cooling.

It is largely used in the manufacture of paints and enamels in place of white lead on account of its permanency and non-poisonous properties, especially for inside work.

Its covering power is superior to that of white lead, but its obscuring power is nothing like so good. Further, zinc paints do not dry so readily, or give such hard and tough elastic films as those given by white lead, and their wearing properties are not so good.

When exposed to severe atmospheric influences it is found that in course of time the zinc paints chalk and rub off, whilst lead paints under the same conditions are considerably more permanent.

It is largely used both in oil and water by artists under the name of Chinese white.

Zinc oxide rapidly darkens in the presence of alcohol on exposure to sunlight. This peculiar property, which appears to be little known, renders paints made on a zinc oxide basis unsuitable for painting compasses in which alcohol is used—*e.g.* airship compasses—unless the paint is covered with an insoluble varnish to protect it from the action of the alcohol.

Zinc oxide is sold under the following marks, *viz.*, White Seal, Green Seal, Red Seal, Yellow Seal, Grey Seal. The last-named contains metallic zinc. The White Seal and Green Seal zinc oxides are remarkably pure, and contain, as a rule, over 99 per cent. of zinc oxides.

SCHEME FOR THE ANALYSIS OF ZINC OXIDES

1. *Insoluble.*—Dissolve 1 gm. in dilute hydrochloric acid by gently warming. If there is any residue, filter off, wash and ignite. Test for barium sulphate and silica.

2. *Total Zinc.*—Make up the zinc solution to 250 c.c., and pipette out 50 c.c. Add 25 c.c. of chloride solution (see below), together with 50 c.c. of distilled water. Boil up in a conical flask, and when just boiling add two to three drops of ferric

chloride solution (about 1 per cent.). Then proceed to titrate with standard solution of potassium ferrocyanide.

At first a blue precipitate is formed, which after the neutral point is passed changes to a pale green.

It is important that the solution should be kept as near to boiling-point as possible in order to ensure a fine end reaction; also that the flask be continually shaken while the titration is proceeding.

It is also advisable to go a little past the neutral point, and titrate back with a standard solution of zinc chloride. Calculate to zinc oxide (ZnO).

The chloride solution mentioned above is simply ammonium chloride and hydrochloric acid in water in the following proportions:—

53.5 gms. NH_4Cl ,
36.5 gms. HCl ,

and made up to 1 litre with distilled water.

Alternative Method (using uranium nitrate as an outside indicator).—Make up a solution of potassium ferrocyanide containing 21.55 gms. per litre. Standardise thus:—

Weigh out 0.2 gms. pure zinc; dissolve in hydrochloric acid (1 : 2) in a 400 c.c. beaker. Dilute and make faintly alkaline with ammonia. Again acidify with hydrochloric acid and add 3 c.c. of conc. hydrochloric acid in excess. Dilute to 250 c.cs. and heat to boiling-point. Titrate hot as follows:—

Reserve about one-third of the zinc solution. Titrate the remainder by running in a few c.cs. at a time till a drop tested on a porcelain tile with a drop of 15 per cent. uranium nitrate solution gives a brown coloration. Now add the greater part of the reserved portion, and titrate more cautiously until the end point is passed. Finally add the rest of the reserved quantity, rinsing the beaker with a large part of the solution from the titration vessel.

Finish very carefully, testing after every addition of two drops. It is well in each test to take out several drops of the zinc solution when the end point is being approached.

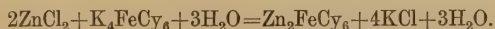
When a brown tinge appears on the indicator, note the burette reading and wait one or two minutes, and see that one of the earlier tests has not developed colour.

The end point is always passed by a drop or two; correct the burette reading accordingly. Correct it also for the amount of ferrocyanide needed to give colour under the same conditions when no zinc is present (one drop as a rule).

Roughly 1 c.c. of standard solution equals 0.005 gms. zinc or 0.006 gms. of zinc oxide.

Now dissolve .5 gms. of the sample of zinc oxide under analysis in 50 c.cs. dilute hydrochloric acid, and proceed as given above.

The above method for the volumetric estimation of zinc in zinc oxide depends on the formation of zinc ferrocyanide according to the following equation:—



The zinc oxide may also be estimated gravimetrically by precipitating either as the sulphide or carbonate of zinc and igniting to zinc oxide.

3. *Calcium*.—If present may be estimated by precipitation with ammonia and ammonium oxalate after the removal of the zinc by ammonia and ammonium sulphide.

4. *Lead*.—Dissolve 1 gm. in dilute hydrochloric acid (filter off any insoluble if necessary); evaporate nearly to dryness on a hot plate. Cool and add 25 c.cs. dilute sulphuric acid and evaporate again till sulphur trioxide fumes are evolved, showing that all the hydrochloric acid has been expelled. Cool; add 25 c.cs. cold water and 25 c.cs. alcohol, and leave for two hours to allow all the lead to precipitate out. Filter through a weighed Gooch crucible. Wash well with 50 per cent. alcohol till free. Dry and gently heat over a low Bunsen burner and weigh as lead sulphate.

SPECIFICATION FOR ZINC OXIDE

1. The zinc oxide must be a pure sublimed zinc oxide, and free from any adulterant or foreign matter.

2. It must be of a pure white colour, and soft in texture.

3. It must be free from metallic zinc and contain not less than 98 per cent. zinc oxide, or more than 1 per cent. of lead expressed as lead oxide.

4. It should not contain more than 0.5 per cent. of moisture, or matter soluble in water.

5. It must not darken on exposure to sulphuretted hydrogen.

Note.—Sometimes a lead-free zinc oxide is required for special purposes such as for paints for lyddite shells. In this case it is customary to specify a zinc oxide containing not less than 99 per cent. of zinc oxide, and not more than 0.2 per cent. of lead or lead compounds calculated to metallic lead.

The small traces of "soluble" lead in these cases are estimated according to the official test as follows:—

A weighed quantity of the sample is continuously shaken for one hour at room temperature with 1000 times its weight of 0.25 per cent. of hydrochloric acid. The mixture is allowed to stand for one hour, and is then filtered. The lead contained in an aliquot portion of the clear filtrate is then precipitated as lead sulphide and weighed as lead sulphate.

LITHOPONE

(Enamel White, Porcelain White, Charlton White, Orr's White, Griffiths' or Knight's Patent Zinc White.)

Lithopone is a white pigment consisting of a mixture of blanc-fixé and zinc sulphide. This pigment was first patented by Orr in 1874, and the manufactured product was called Zinkolith, or Orr's Zinc White.

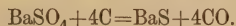
The process for the manufacture of this pigment is still carried on at Orr's Zinc White Company's Works at Widnes, Lancashire.

White pigments of a similar composition were introduced by Griffiths in 1875 and by Knight in 1876.

Lithopone is now manufactured in immense quantities for use as a pigment in the paint trades as a non-poisonous substitute for white lead in Germany, Holland, Belgium, the United States and England.

The process of manufacture varies considerably in the many different works engaged in the production of this extremely valuable white pigment, but the main essentials of the process are based upon the following reactions :—

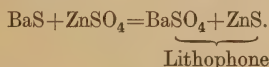
1. Barium sulphide is first prepared by calcining finely ground barytes (Heavy Spar BaSO_4) with charcoal, coke or coal in retorts at a white heat ; the calcined mass is then dropped into water and lixiviated to dissolve out the barium sulphide—



2. The next operation consists in making up a weak solution of zinc sulphate, care being taken to see that it is perfectly free from iron. This solution is run into the solution of barium sulphide with continual stirring till a slight excess of zinc sulphate remains over. The precipitate of barium sulphate and zinc sulphide thus formed is well washed by decantation till perfectly free, then filter-pressed and dried at about 50°C .

The dried mixture thus obtained is of a greyish-white colour, and of a very harsh texture.

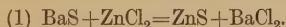
The reaction that takes place may be expressed thus :—



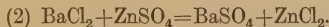
3. The crude dry lithopone is next calcined at a dull red heat in special furnaces, and the red-hot mass raked out into iron tanks containing cold water. This sudden cooling in cold water of the calcined material causes it to become softer in texture, and also makes it denser and thus have more body.

The cooled mass is next thoroughly ground under water till perfectly fine ; it is then pressed and dried.

An alternative method which is carried out in some works consists in precipitating the barium sulphide with a solution of zinc chloride thus :—



A solution of zinc sulphate is next added whereby barium sulphate is precipitated thus :—



The zinc chloride thus set free can be used to precipitate more zinc sulphide by the fresh addition of barium sulphide addition, as in equation (1).

The advantage of this process consists in the fact that the proportion of barium sulphate to zinc sulphide can be regulated at will according to the grade of lithopone desired.

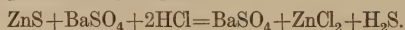
Properties and Uses.—Lithopone is of a good white colour and is soft in

texture. It has excellent body and density, although not equal to white lead in this respect. Its specific gravity is 4.3.

It is non-poisonous, and on account of this, and also because its cost is only about half that of zinc oxide and white lead, it has gradually come more and more into favour as a pigment, till at the present time the yearly consumption is enormous.

It requires about 12 per cent. of oil to grind it into a stiff paste. It is largely used as the basis of many of the cheaper dark-tinted paints such as slate greys and so on.

Lithopone is insoluble in water, but is readily attacked by even dilute acids, with evolution of sulphuretted hydrogen.



Lithopone

It is not affected by sulphur gases. Unfortunately lithopone has two serious defects, which greatly impede its still more extended use. The first is its instability as regards light. In the presence of sunlight it rapidly darkens, gradually turning grey, then black. On leaving in the dark it regains its white colour.

The second defect is that when this pigment is made up into paint form, and used for the protection of outside structures, it wears very badly, and after twelve months' exposure chalks and flakes off. Moreover, in iron structures, owing to the decomposition of the zinc sulphide, acids are formed which cause corrosion.

This darkening property of lithopones has been the subject of very much patient investigation by many chemists, and many patents have been taken out with the object of preparing lithopones fast to light.

It is now supposed that the darkening of lithopones can be ascribed to the presence of a small proportion of chlorides, and several processes are now in operation whereby lithopones more or less fast to light are produced.

Eibner ("Chemiker Zeitung," February 1923) states that the well-known darkening action of sunlight on lithopone is due to phosphorescence of the ignited zinc sulphide, caused by the presence of impurities in the shape of small quantities of foreign metals. These react with the zinc sulphide in the presence of sunlight, forming coloured sulphides, which subsequently oxidise, thus restoring the original colour. The presence of lead, manganese and copper causes the pigment rapidly to become grey; iron, nickel and cobalt have the same effect, but the colour takes much longer to develop. Manganese alone produces brown tints; cadmium, yellowish tints; and thallium and antimony salts, first reddish tints, then a grey or black discoloration. Long ignition of the lithopone in the process of manufacture results in a product containing up to 2 per cent. of zinc oxide, and this accelerates the rate of oxidation of the foreign metals to white or more feebly-coloured compounds, but does not prevent darkening first occurring. The latter effect is accelerated by the presence of water or chlorine compounds; the latter especially are objectionable, as they result in the impurities being converted into chlorides, which in the presence of light are quickly converted into sulphides, producing much greater discoloration than if chlorides are absent. Lithopone absolutely free from foreign metals shows no discoloration at all, even if chlorides

are present. A satisfactory purification of the zinc solution previous to treatment with barium sulphide is obtained by treating it with ammonia to dissolve the zinc hydroxide first precipitated, filtering and boiling with zinc dust. In this way iron, manganese, lead, cadmium, copper, thallium, nickel, and cobalt are completely removed, and the lithopone made from this solution is absolutely fast to light.

Ostwald & Brauer, according to a German patent (D.R.P. 202709), conduct the calcination process in closed vessels, or in vessels through which inert gases free from oxygen are passed, and lixiviate the red hot mass in water which has been previously well boiled to remove all air.

Bayer & Company's process consists in treating the finished lithopone in water containing a small percentage of alkaline sulphate or chlorides through which an electric current is passed.

Lithopone comes on to the market usually as 30 per cent. Red Seal Brand, the average composition of which, according to many analyses made by the author, is as follows :—

	German Red Seal Lithopone.	Dutch Red Seal Lithopone.
Barytes (BaSO_4)	69.92	70.10
Zinc sulphide (ZnS)	29.51	26.60
Zinc oxide (ZnO)	0.57	3.30
	<hr/> 100.00	<hr/> 100.00

Other brands which also come on to the market to a much lesser extent are :—

Green Seal containing 40 per cent. ZnS	
“ “ “ 34 “ “	
“ “ “ 32 “ “	
White “ “ 26 “ “	
Blue “ “ 22 “ “	
Yellow “ “ 15 “ “	

The covering power and body of lithopone vary according to the amount of zinc sulphide they contain. The higher the contents of zinc sulphide the greater the body and covering power, and vice versa.

In some of the poorer grades of lithopone finely ground natural barytes is mixed in place of the precipitated blanc-fixé made during the process, but this has serious disadvantages as regards the texture and body of the finished product.

Sulfozone.—A white pigment has been marketed under the name of sulfozone as an alternative to lithopone. It consists of a mixture of calcium sulphate and zinc sulphide.

ANALYSIS OF LITHOPONE

Moisture.—(1) Heat 2 gms. at 105°C . till constant in weight. Loss in weight equals the moisture.

(2) *Barium Sulphate* (BaSO_4).—Boil 1 gm. with diluted hydrochloric acid

till no more sulphuretted hydrogen is evolved. Filter, wash well and ignite. The residue equals the barium sulphate (BaSO_4).

Note.—If the lithopone is treated with dilute sulphuric acid in place of hydrochloric acid the author finds that the weight of the residue (BaSO_4) obtained is always 0.5 to 1 per cent. higher. This is due to the slight solubility of the barium sulphate in dilute hydrochloric acid.

(3) *Total Zinc.*—Add slight excess of ammonia to the filtrate from the barium sulphate, then add hydrochloric acid till acid. Bring nearly to the boil and titrate with standard potassium ferrocyanide as described under zinc oxide (page 51).

The zinc may also be estimated by precipitating the solution from the barytes with excess of soda carbonate (anhydrous) and igniting the zinc carbonate thus obtained to zinc oxide.

(4) *Zinc Sulphide* (ZnS).—Boil 1 gm. with hot nitric acid to which a few crystals of potassium chlorate have been previously added, and evaporate down to small bulk. Dilute and add barium chloride solution. Filter, wash, and ignite. Equals barium sulphate.

$$\text{BaSO}_4 \times 0.1373 = \text{weight of sulphur.}$$

Calculate sulphur to zinc sulphide.

An alternative method consists in fusing 1 gm. of the sample with 5 gms. of a mixture of potassium nitrate and potassium chlorate for one hour. Extract the fused mass with hot dilute nitric acid and precipitate as above.

(5) *Zinc Oxide* (ZnO).—Calculate this by subtracting the zinc found as zinc sulphide from the total zinc in (3) and calculating to zinc oxide.

(6) *Calcium.*—Separate the zinc by ammonia and ammonium sulphide and precipitate with ammonium oxalate in the usual manner. Calculate to calcium sulphate.

SPECIFICATION FOR LITHOPONE (30 per cent.)

The lithopone must be of a good white colour and fine in texture, and free from coarse particles.

It must consist of a mixture of approximately 30 per cent. sulphide of zinc and 70 per cent. of precipitated barytes.

It must not darken on exposure to sulphuretted hydrogen or on exposure to sunlight.

It must contain not more than 0.5 per cent. of moisture or matter soluble in water.

TITANIUM WHITE

(Titanium Dioxide (TiO_2).)

Titanium was discovered in 1791 by the Rev. William Gregor while investigating the magnetic sand (menachanite) found in Menachan (Cornwall). He called this element "menachin."

It was subsequently investigated in 1795 by M. H. Klaproth, who found what he thought to be a new metal in rutile and called it titanium (derived from "Titans," the fabled giants of ancient mythology). In 1797 Klaproth proved that titanium was identical with the menachin of Gregor.

Titanium is not found in nature free, but combined it occurs as the dioxide (TiO_2) in three minerals, rutile, brookite, and anatase, each of which possesses different crystalline forms.

Titanium also occurs widely distributed in the minerals ilmenite (FeTiO_3), titaniferous iron ore, and sphene or titanite (calcium titanium silicate) (CaTiSiO_5), that is CaO , TiO_2 , SiO_2 .

Titanium white (TiO_2) is manufactured for use as a white pigment from the mineral ilmenite, which, as stated above, is a compound of iron oxide and titanium dioxide (FeO, TiO_2), vast deposits of which are found on the west coast of Norway.

The manufacture of this white pigment is carried out by the Titan Co. of Norway according to the following process.

Finely pulverised ilmenite is mixed with ordinary concentrated sulphuric acid. The mass is heated whereby a violent reaction between the acid and the ilmenite takes place under coagulation of the mass, thus transforming the titanium and iron contents of the ore into titanium and iron sulphates.

The coagulated mass is afterwards dissolved in water and freed from undecomposed minerals through a settling process.

The clear solution containing the iron and titanium sulphates is afterwards heated to a boiling temperature by means of indirect steam which causes the titanium to precipitate in the form of titanium hydrates, chiefly meta-titanic acid. The titanium precipitates thus obtained are washed until free from iron. The precipitate contains a small quantity of absorbed sulphuric acid, and small quantities of basic sulphates of titanium which are neutralised by the addition of barium carbonate.

The neutralised precipitate is afterwards calcined to remove the water of hydration and to convert the titanium dioxide into a crypto- or micro-crystalline condition.

This white pigment is marketed under the name of titanium white, and is essentially titanium dioxide (TiO_2), containing only a minimum proportion of barium sulphate.

Reduced titanium whites, or the so-called "composite pigments," are also manufactured and are prepared by precipitating the titanium dioxide on a barium sulphate base.

The process for the manufacture of the composite pigments is broadly as follows :—

Ilmenite is smelted in an electric furnace with fluxes whereby a titanium concentrate is produced, which is afterwards dissolved in sulphuric acid. This forms a solution of titanium sulphate comparatively free from iron, most of the iron having been eliminated in the smelting process.

The titanium sulphate solution is mixed with blanc-fixé and the mass boiled

by direct steam, thereby precipitating titanium hydrates upon a base of blanc-fixé, so that a mutual absorption of the two compounds takes place.

By subsequent calcination the amorphous precipitate is converted into the crypto-crystalline or micro-crystalline state, whereby the two compounds are so to say coalesced.

After calcination the titanium pigment is very carefully pulverised and air-floated so as to yield a product of the highest possible fineness and uniformity.

Properties and Uses.—Titanium white (TiO_2) has a brilliant white colour and is extremely fine in texture. Its specific gravity ranges from 4.0 to 4.3. It requires about 23 per cent. of oil to grind it into a stiff paste.

Titanium white is quite inert and is not affected either by heat, acid, or sulphur fumes. It is non-poisonous. Paints made with it are exceptionally durable on exposure and retain their colour under all conditions.

The pigment has exceptional body and covering power, and paints made with pure titanium white have, bulk for bulk, nearly twice the opacity or obscuring power of paints made with pure white lead.

Owing to its complete inertness it exerts no drying influence upon the oil or varnish with which it is ground, so that the paint film obtained on drying (on the addition of dryers) is rather soft and apt to pick up dust.

This defect is entirely prevented by the addition of 10 to 25 per cent. of oxide of zinc which hardens the film, thus preventing discoloration by the accumulation of dust or dirt.

The cost of titanium white—which is about twice that of zinc oxide or white lead—is a serious impediment to its more extended use in the paint industry, but there is little doubt that, provided its cost of production can be considerably reduced, it will come largely into use, and be a valuable addition to our present white pigments.

ANTIMONY OXIDE

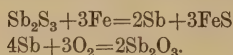
(Antimony White.)

White antimony oxide, or antimonious oxide (Sb_2O_3), has been introduced of recent years as a substitute for white lead on account of its non-darkening and non-poisonous properties.

When metallic antimony is burnt in contact with air or oxygen the fumes evolved consist of antimonious oxide.

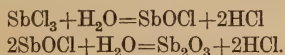
The raw material used in the manufacture of antimony oxide is stibnite, or grey antimony (Sb_2S_3).

The naturally occurring stibnite, either alone or mixed with iron, is roasted in the presence of air whereby the antimony oxide thus formed is converted into a fume or vaporised, and collected in much the same manner as zinc oxide.



When native antimony sulphide is dissolved in hydrochloric acid, sulphuretted

hydrogen is evolved, and antimony trichloride formed. If water is added to the antimony trichloride the oxychloride (SbOCl) is precipitated, and by prolonged digestion, this is transformed into antimonious oxide.



Algorath powder has the composition approximately of $\text{SbCl}_3 + \text{Sb}_2\text{O}_3$.

Properties and Uses.—Antimony oxide when carefully prepared for use as a pigment is of a pure white colour.

Its specific gravity is about 5.4, which is approximately that of zinc oxide; it differs however from zinc oxide in that it requires only about 10 per cent. of oil to grind it into the form of a stiff paste.

It is of a fine crystalline nature, and exceedingly soft and “buttery” in texture.

Antimony oxide is very slightly soluble in water, but wholly soluble in hot concentrated hydrochloric acid.

Antimony oxide paint films turn yellow in the presence of sulphuretted hydrogen, but on exposure to pure air and light regain their original colour. Under ordinary atmospheric conditions this oxide retains its colour better than white lead.

On account of its non-toxic properties it is used as a substitute for white lead, especially in France, where, owing to the prohibition of the use of the latter material, very large quantities are brought into consumption.

Antimony oxide differs from zinc oxide and white lead inasmuch as it is an acidic pigment, and also has no accelerating effect on the drying of linseed oil such as is the case with white lead. On account of its inert character it has, unlike zinc oxide, no thickening or “feeding” action on varnishes.

Paints made up from antimony oxide are rather slow drying, and tend to give soft films; this, as with titanium white, may be overcome by the addition of a percentage of zinc oxide.

The opacity of antimony oxide paints is equal to that of lithopone; and under weathering influences its durability has been shown to approximate to that of white lead.

TIN OXIDE (SnO_2)

Tin oxide or tin white is a white powder, which may be prepared by heating metallic tin in the air; also by the action of nitric acid.

If metallic tin is dissolved in concentrated nitric acid and poured into water, a dense heavy white powder of tin hydroxide is produced ($\text{Sn}(\text{OH})_2$).

Tin oxide is insoluble in water and acids, and is used for colouring glass (opal glass) and in vitreous enamels.

CHAPTER VII

THE YELLOW INORGANIC PIGMENTS

(A) THE YELLOW EARTH COLOURS

1. YELLOW OCHRE, OCKER, CHINESE YELLOW

THE natural yellow ochres occur very widely distributed in various parts of the earth. The best known and purest varieties are the French, English and Spanish ochres. They owe their yellow colour to the fact that they contain hydrated ferrous oxide.

Preparation.—The natural occurring crude ochres are prepared for use in the pigment industry by grinding and levigation, as by this means the coarser and heavier particles are separated from the lighter material.

Levigation.—This process, which is largely used in the separation of the heavy and coarser silicious particles from the finer material, will be briefly described here as it is applicable to all the earth colours; and although the oldest form of separation known, is still by far the simplest and cheapest method available.

The earth colours as they are dug up are emptied into huge wooden or stone tanks, built usually into the slope of a hill, mixed with water from a stream and stirred either by hand or mechanically. By this means the heavier and coarser particles separate to the bottom whence they are from time to time removed. The stream of water which is continually flowing in washes away the finer particles into two or three series of tanks (each series generally consisting of four or five tanks), each succeeding tank being larger than the previous one. In this way the first series of tanks is eventually completely filled with the muddy liquor, the last and largest tank containing the finest grades. The stream of water is now diverted to the second series of tanks and the same operation repeated whilst the first series is settling out.

After settlement the clear water is run off and the fine ochre is dug out and allowed to dry in the sun or by the aid of artificial heat in 12–20 feet long kilns.

In more modern works the sludge is pumped out and filter pressed to remove the excess of water, and then dried.

In some cases the earthy material receives a preliminary grinding under water in edge runners so as to grind out the heavier particles. It may be of interest to mention here that one of the French firms engaged in the ochre industry mine

100,000 tons of ochre annually, out of which only about 20,000 tons are suitable for the paint trade.

Recently the Plauson colloid mill has been introduced, by means of which particles of colloidal fineness are produced by centrifugal force.

This process will undoubtedly be largely used in the near future for the production of pigments which are required to be in a state of extremely fine division for use in the paint industries.

The Plauson Colloid Mill (see Figs. 11 and 12) consists essentially of a strong circular cast-iron body. The body is double cased to provide for heating or cooling, and has suitable branches fitted with baffles for filling the machine with solids and liquids.

In the lower part of the body there is a shaft which is designed to run at about 3000 r.p.m. This revolving shaft has steel blades or beaters attached, which rotate between two sets of blades or anvils fixed to the body.

Perforated baffle plates are arranged coaxially with the beater shaft to reduce needless friction of the material, openings being left for the material being treated.

As liquid is necessary for the operation of the mill, dry grinding cannot be carried out.

The chief grades of ochre which come on to the English market are :—

- (1) The French Ochres : Golden Ochre, J.F.L.S., J.F.L.E.S., J.F.L., J.C., etc.
- (2) Native Oxford Ochre, Stone Ochre.
- (3) Spanish Ochre and Italian Ochre.
- (4) Indian Ochres.

Very often a poor coloured ochre is toned up by the addition of a little chrome yellow to improve its colour, and the author has even come across ochres to which a small percentage of yellow acid dyestuff has been added with the same object.

Properties and Uses.—These pigments are soft in texture and extremely permanent. Their covering power is moderately good. They are largely used as stainers and for graining work. On ignition they lose their water of combination and turn red, owing to the conversion of the yellow ferrous hydrate into ferric oxide.

The specific gravity is about 2.80, but varies according to the grade, some grades being as high as 3.20.

Strength.—To test the strength of an ochre reduce with ten times its weight of zinc oxide in linseed oil, and then compare with standard ochres similarly reduced. The percentage of iron is also a guide as to the strength and covering power of an ochre.

Oil Absorption.—The amount of oil required to grind an ochre into a stiff paste is a factor of considerable importance in the manufacture of paints, and this should always be determined when selecting an ochre, and the amount of oil found to be necessary checked against that of the standard ochre.

Method.—Weigh out 1 gm. of the ochre on to a porcelain slab, and drop from a burette raw linseed oil on to same, working up the ochre all the while with a

palette knife. Stop adding the oil at the point where the ochre is just converted into paste form, and count the number of drops used.

Specification.—The usual specification required for a good class of prepared ochre is as follows :—

It must be of a good bright yellow colour and consist of a levigated natural hydrated silicate of aluminium containing iron compounds equal to not less than 20 per cent. sesquioxide of iron (calculated as Fe_2O_3) and also contain not more than 5 per cent. of calcium compounds in any form. Further, it must not contain more than 0.5 per cent. moisture. It must be perfectly fine and free from grit, and all pass through a 120-inch mesh sieve.

It must be free from barium sulphate or any added matter, also from any brighteners or toners such as chromate of lead or aniline dye-stuffs.

Analysis of Ochres.—The general scheme for the analysis of ochres is as follows :—

Moisture.—Weigh out 5 gms. in a watch glass and heat at 105°C . for two hours. Loss equals the moisture.

Combined Water.—Gently heat 2 gms. of the above dried sample in a weighed platinum crucible over a slow bunsen flame till constant. The ochre turns red and the loss in weight gives the combined water.

Barytes and Silica.—Take 1 gm. of the ochre and boil up on a hot plate with 100 c.c. conc. hydrochloric acid. Evaporate to dryness to render the silica insoluble. Add more hydrochloric acid and again evaporate down to small bulk. Filter off the insoluble matter, wash residue (which should be white, showing absence of iron), and ignite gently. The residue should consist of silica only. Test for barytes with the platinum wire ; if present it is an adulterant, and may be estimated by removing the silica by treating with hydrofluoric acid in the usual way.

Lead.—Dilute well and pass in hydrogen sulphide. A black precipitate indicates lead. Filter off, wash, dissolve, add sulphuric acid (H_2SO_4) and weigh as lead sulphate and calculate to chromate of lead (see Chromed Ochres). Boil, filtrate to remove hydrogen sulphide, add ammonia. Filter and wash the precipitate well.

Ferric Oxide.—Dissolve the filtrate in hydrochloric acid, make up to 250 c.c., and estimate the iron in 50 c.c. of this solution with standard bichromate of soda in the usual way.

Alumina.—Pipette out another 50 c.c. and estimate alumina and iron by re-precipitating, ignite, weigh and calculate. The difference equals Al_2O_3 . If lead is present the chromium must be separately estimated.

Calcium.—The calcium in the filtrate is estimated from the iron precipitate by precipitation with ammonia and ammonium oxalate, and calculated either to carbonate or sulphate of calcium.

Magnesium.—The magnesium is estimated as magnesium pyrophosphate. Carbon dioxide is estimated by treating 1 gm. in the Schrötter apparatus, and sulphuric acid is estimated by precipitation with barium chloride. Calculate to carbonate and sulphate of lime.

The following typical analyses (by the author unless otherwise stated) will

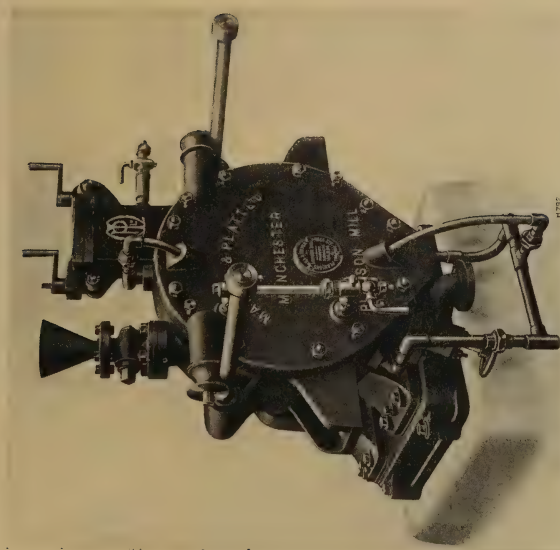


FIG. 11.—PLAUSON COLLOID MILL (FRONT VIEW).

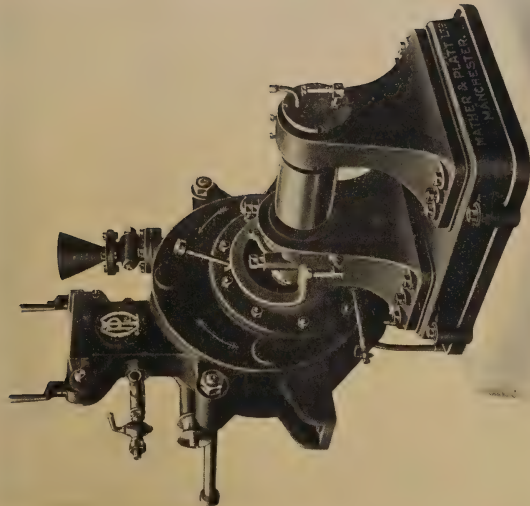


FIG. 12.—PLAUSON COLLOID MILL (BACK VIEW).

indicate the general composition of the ochres which are placed on the market in this country :—

(1) *Ochre, French J.F.L.S.*

Moisture . . .	0.50 per cent.
Comb. water . . .	8.90 "
Silica (SiO_2) . . .	52.00 "
Ferric oxide (Fe_2O_3) . . .	22.50 "
Alumina (Al_2O_3) . . .	12.70 "
Lime (CaO) . . .	3.00 "
Undetermined . . .	0.40 "
	<hr/> 100.00

(2) *French J.C. Ochre.*

Moisture . . .	0.70 per cent.
Comb. water . . .	9.20 "
Silica (SiO_2) . . .	65.50 "
Ferric oxide (Fe_2O_3) . . .	12.50 "
Alumina (Al_2O_3) . . .	8.50 "
Lime (CaO) . . .	2.50 "
Undetermined . . .	1.10 "
	<hr/> 100.00

(3) *French Prepared Ochre (G. H. Hurst).*

Water, hygroscopic . . .	1.80 per cent.
Water, comb.	9.20 "
Silica (SiO_2)	54.00 "
Alumina (Al_2O_3)	13.75 "
Ferric oxide (Fe_2O_3)	20.73 "
Calcium oxide (CaO)	0.19 "
	<hr/> 99.67

(4) *Stone Ochre.*

Water, hygroscopic . . .	0.50 per cent.
Water, comb.	4.20 "
Silica (SiO_2)	30.70 "
Barytes (BaSO_4)	25.20 "
Ferric oxide (Fe_2O_3)	9.40 "
Calcium carbonate (CaCO_3)	28.40 "
	<hr/> 98.40

Note.—This analysis of the stone ochre shows that it is not a genuine ochre, but has been adulterated largely by the addition of barytes and Paris white.

(5) *Extra Strong Bright Golden Ochre.*

Moisture	2.10 per cent.
Loss on ignition	11.20 "
Silica (SiO_2)	52.30 "
Ferric oxide (Fe_2O_3)	30.40 "
Alumina (Al_2O_3)	4.00 "
	<hr/> 100.00

(6) *Spanish Ochre.*

Loss on ignition	6.87 per cent.
Silica (SiO_2)	11.50 "
Ferric oxide (Fe_2O_3)	56.05 "
Alumina (Al_2O_3)	5.55 "
Calcium carb. (CaCO_3)	18.93 "
Magnesium oxide (MgO)	1.10 "
	<hr/> 100.00

(2) RAW SIENNA, TERRA DI SIENNA

The siennas are not so widely distributed as the ochres, to which they have a certain resemblance. The chief source of supply of this valuable pigment is Italy, from which country by far away the best grades come. A certain amount is also obtained from Germany and America.

Preparation.—By grinding and levigation in a similar manner to that described under Ochres.

Properties and Uses.—Raw siennas have a deeper yellowish tone than the ochres. Their colour varies slightly according to the locality from which they are obtained. They are exceedingly transparent, and on this account are chiefly employed as stainers and for graining work.

In selecting a sienna the undertone and transparency should not be overlooked.

Those that are "muddy" should be rejected, and only those grades should be accepted which are bright, transparent and clean on reduction.

Analysis.—See under Ochres.

The following analysis of an Italian and a German prepared raw sienna by the author will give a clear idea as to their composition :—

<i>German Raw Sienna, Ex S.</i>			<i>Italian Raw Sienna, Ex G.</i>		
Moisture	0.70	per cent.	Moisture	1.20	per cent.
Loss on ignition	12.50	"	Loss on ignition	20.40	"
Silica (SiO_2)	11.50	"	Silica (SiO_2)	9.70	"
Ferric oxide (Fe_2O_3)	70.40	"	Ferric oxide (Fe_2O_3)	55.40	"
Alumina (Al_2O_3)	2.00	"	Alumina (Al_2O_3)	8.00	"
Manganese dioxide	0.70	"	Manganese dioxide	0.30	"
Calcium oxide (CaO)	2.20	"	Calcium sulphate	5.00	"
	<u>100.00</u>			<u>100.00</u>	

Specification.—The raw sienna must be a finely levigated natural earth colour in a fine state of sub-division, and free from any coarse particles. It must contain not less than 50 per cent. of iron (calculated as Fe_2O_3). It must also contain not more than 1.5 per cent. of moisture. It should be free from any added materials such as barytes, silica, Paris white, terra alba, etc.

Burnt Sienna is obtained by calcining the raw sienna at a low temperature till the desired shade is produced.

Properties and Uses.—Burnt sienna possesses a deep orange red colour, with a blood-red undertone. It is a beautiful transparent colour, and is very largely used as a stainer. Burnt siennas heavily reduced with silica and coloured with magenta to give them a rich undertone are frequently offered on the market.

Strength Test.—The strength test of both raw and burnt sienna is carried out by reducing by 1 : 10 with zinc oxide in linseed oil.

Specification.—See Raw Sienna.

The following analyses, by the author, of an Italian and a German raw sienna, made after calcining, will indicate the changes the raw materials undergo :—

¹ <i>German Burnt Sienna, Ex S.</i>			<i>Italian Burnt Sienna, Ex G.</i>		
Moisture	.25	per cent.	Moisture	..	
Loss on ignition	2.05	"	Loss on ignition	8.80	per cent.
Silica (SiO_2)	13.55	"	Silica (SiO_2)	20.00	"
Ferric oxide (Fe_2O_3)	79.22	"	Ferric oxide (Fe_2O_3)	65.05	"
Aluminium oxide (Al_2O_3)	1.58	"	Aluminium oxide	5.20	"
Manganese dioxide	.91	"	Manganese dioxide	.45	"
Calcium oxide (CaO)	1.99	"	Calcium sulphate	.50	"
	<u>99.55</u>			<u>100.00</u>	

¹ *Note.*—This German sienna was one of the best the author has ever come across. It had great strength and transparency, and the undertone was of a deep blood-red colour.

(B) THE YELLOW INORGANIC CHEMICAL COLOURS

1. CHROME YELLOW

(Chromate of Lead, Chromgelb, Jaune de Chrome.)

This group of colours, commonly known as the "Chromes," is by far away the most important of the yellow pigment colours at the disposal of the paint manufacturer. Their value is due not only to their remarkably good body and covering power, but also to the fact that by their aid an immense range of bright shades can be obtained, varying, according to the method employed in their manufacture, from the palest yellow (Primrose Chrome) to the deepest red shade (Derby Red or Persian Red).

Moreover, in conjunction with Brunswick blues they give a wonderful variety of strong bright greens known as the Brunswick greens, which are manufactured in enormous quantities at the present time.

The various chrome substitutes made from synthetic dyestuffs which have been placed on the market have not been able to take the place of the "Chromes" to any appreciable extent on account of their high price and lack of body.

The Hansa yellows and similar types of synthetic colours (see Lakes and Lake Pigments, Chapter XIII.), in consequence of their great stability and permanency, will, no doubt, in course of time come more and more into favour as chrome substitutes, provided their cost of production can be reduced so as to put them on to a competitive basis with the "Chromes."

Manufacture of Chrome Yellow.—If a cold dilute solution of chromate or bichromate of potash or soda is run into a cold solution of a soluble lead salt such as nitrate or acetate of lead, pale bright yellow precipitate of chromate of lead is produced according to the following equation :—



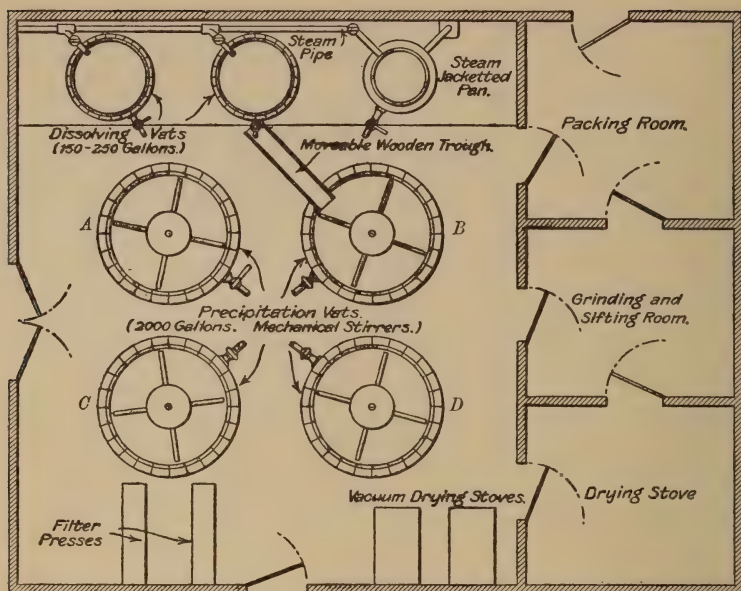
If this yellow precipitate of chromate of lead is next vigorously boiled with an alkali such as caustic soda or lime, a basic chromate of lead is produced thus :—



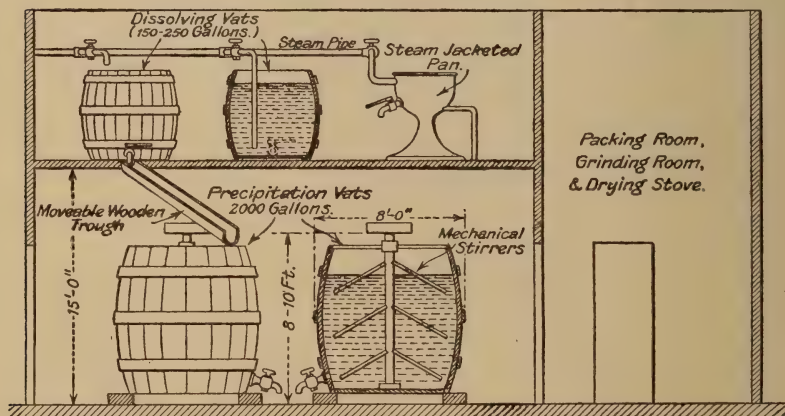
On these two simple reactions the whole manufacture of chromes is based. The raw materials used by the colour manufacturer in the production of his chromes are :—

- (1) Bichromates of soda and potash.
- (2) Nitrate and acetate of lead.

In the early days of the manufacture of chromes it was necessary, owing to their being no bichromates on the market, for the colour maker to manufacture his own bichromate of potash from chrome iron-stone (FeCr_2O_4), and this he did by fusion in a reverberatory furnace with potassium nitrate and subsequent lixiviation with water containing sulphuric acid. This has now fallen completely into disuse, as the colour manufacturer finds it more economical and convenient



PLAN OF COLOUR HOUSE.



ELEVATION.

FIG. 13.—PLAN OF COLOUR HOUSE.

FIG. 14.—ELEVATION OF COLOUR HOUSE.

to obtain his supply of bichromates of potash and soda from the chemical works directly engaged in the manufacture of these products.

Colour House Plant.—The modern plant used by the colour maker in the production of his chromes will be described in some detail, as the same plant may also be used for the manufacture of Prussian blue, lake colours, greens, etc.

The first essential in the manufacture of colours is that the colour house should have a plentiful supply of pure soft water. The presence in the water of lime, and especially of iron, is extremely deleterious to the bright shades which it is the aim of the colour maker to produce. The presence of sulphates and chlorides is also very objectionable if present in more than minute quantities. A plentiful supply of boiling water and steam must also be at hand.

The colour house, a plan and elevation of which is shown in Figs. 13 and 14, is generally arranged in two storeys.

On the ground floor are placed a series of large wooden colour or "striking" vats or tubs A, B, C, D (see Fig. 15) having a capacity of 1000 gallons or more according to the sizes of the batches of colour that are going to be produced at one "striking" or precipitation. These vats are about 5 feet high and are provided with mechanical stirrers (Fig 16), the labour of hand-stirring being thereby eliminated. In addition the vats are provided with a series of pegs *a*, *b*, *c*, which can be removed at will; these are used for drawing off the top liquor as the precipitate settles down.

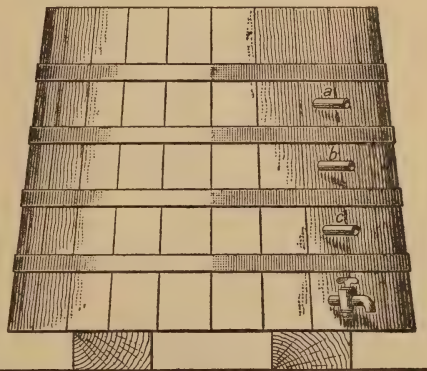


FIG. 15.—PRECIPITATION VAT.

On the top storey, which is often simply a gallery running round the colour house, are placed two or three dissolving tubs of smaller capacity, say about 250 gallons, each provided with three pipes to supply (1) hot water, (2) steam, (3) cold water. The bottom of the dissolving tubs are provided with a large tap fitted with a movable strainer. By means of this tap and strainer the contents of the dissolving tubs can be emptied at practically any speed according to the requirements of the particular colour or shade that is being made. Also at the same time the strainers will remove any undissolved particles or impurities that may be present. By means of a long wooden channel the contents of these vats can be run off into any of the receptacles below at will.

The colour formed in the "striking" or precipitating vats, after washing free from all insoluble matter, is pumped out through a filter press (see Figs. 17 and 17A) and pressed till all the excess of water is removed. In the case of small batches of colour these may be emptied by hand on to cloth strainers, but this is a slow

and cumbersome method. The colour is then removed to the drying-room or vacuum stoves.

The Drying of Pigments.—The drying-room or stove consists of a large brick chamber with solid walls and two doors, the latter of which are of course kept closed during the drying operation. The chamber is fitted up with a convenient series of racks or shelves about 2 feet apart and reaching to the top of the stove; on these are placed the trays, which may be made of wood, iron or aluminium. Space is left between each series of racks to allow the men room for filling and emptying the stove. In addition the chamber is fitted with an electric fan, and a wet and dry bulk thermometer so that the humidity and the amount of air

passing through may be regulated to ensure that the maximum efficiency in drying is obtained.

The heating is arranged either by a series of steam pipes or else by a fire with flues leading round the stoves. Very great care must be taken to see that the temperature of the stove is carefully regulated, as any overheating would result in whole batches of the more delicate colours being spoilt. The temperature of the stove varies from about 100° F. to 150° F. according to the position of the trays from the source of the heat.

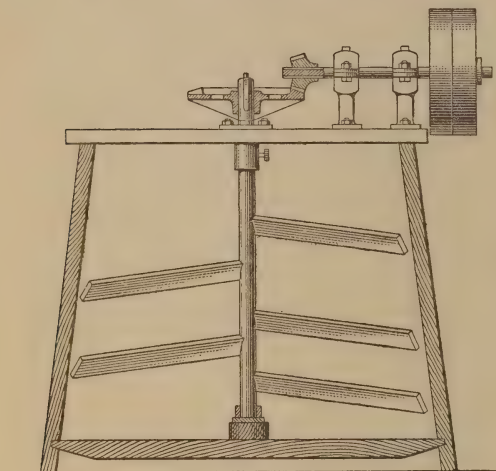


FIG. 16.—PRECIPITATION VAT SHOWING STIRRERS.

Many of the more permanent colours can be dried more expeditiously by the aid of the vacuum stove. The illustration (see Fig. 18) shows a complete Scott vacuum drying installation which consists of a cast-iron chamber built up of heavily reinforced plates, bolted together on machined flanges. To the front of this chamber is fitted a cast-iron door carried on an overhead steel rail on roller bearing arranged so that the door can be moved easily into and out of place. The door has a square section rubber joint carried in undercut grooves and is held in place by steel swing bolts with quick-fitting handle nuts. Inside the chamber are arranged a number of steam-heated coil shelves. Each shelf consists of a single length of tubing very closely pitched and arranged with inlet and outlet branches which pass through the back of the stove and are connected into external steam and drain headers by means of unions and special flanged nuts, the whole being arranged so that the vacuum joint is distinct from the steam joint and there is no

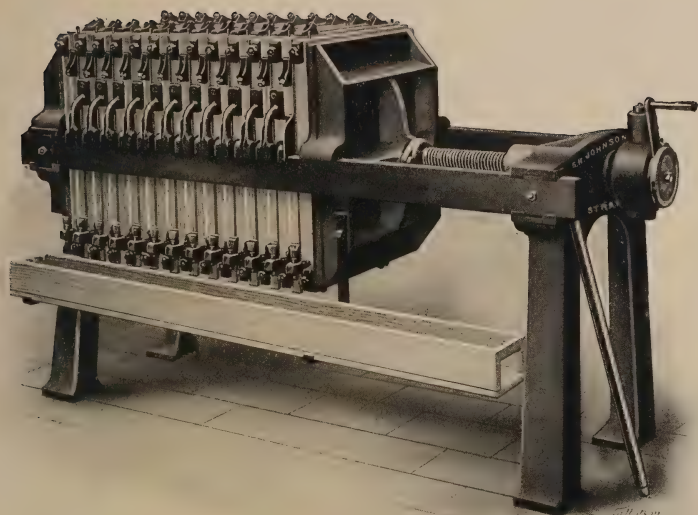


FIG. 17.—TWELVE-CHAMBER WOODEN FILTER PRESS FOR COLOURS; FLUSH PLATE AND DISTANCE FRAME TYPE; PLATES 28 IN. BY 21 IN. THROUGH EXTRACTION WASHING ARRANGEMENT. PLATES FITTED WITH LIGNUM VITÆ COCKS.

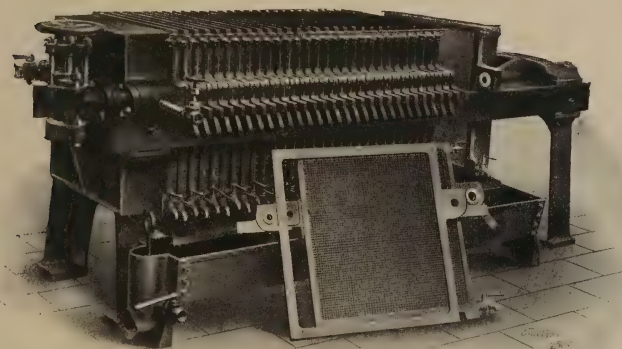


FIG. 17A.—FILTER PRESS FOR COLOURS; 25-INCH SQUARE D TYPE WITH 30 CHAMBERS.
(S. H. Johnson & Co., Ltd.)

possibility of steam leaking into the vacuum chamber. In other words, any steam leak is into the atmosphere and not into the stove. It is quickly detected, and it is possible to attend to either the steam or vacuum joint without removing the shelf. These coil shelves are reinforced and stiffened in a special manner which prevents the movement of the individual pipes when trays are slid into and out of position. In addition this reinforcement stiffens the whole shelf.

In addition to the drying shelves a top heating coil for keeping hot the top of the chamber is provided, thus preventing condensation at this point, with a resulting slowing down of the drying on the top shelf.

Vapour is led from the chamber through the vapour pipe shown and enters a horizontal two-flow condenser (tubular) arranged to give two passages for both the vapour and the condensing water. The condenser is made with contact parts to suit the particular liquid or vapours to be dealt with, and the condensed vapour is concentrated into a drip pipe projecting into the water receiver shown under the condenser. The water receiver is generally in mild steel, but sometimes in cast iron or copper. The internal drip pipe is kept under observation through the round light and sight glasses arranged near the top of the receiver. This enables the progress of the drying operation to be determined, as, of course, towards the end of the drying there is very little condensed solvent issuing from the drip pipe. This receiver is also fitted with gauge glass and fittings, discharge cock and air connection to vacuum pump.

The receiver is made large enough to take the whole of the condensed steam or solvent in a charge of the stove. The condensed liquid is stored in the receiver until the end of the drying operation, and is run away to store or waste when the vacuum on the plant is broken and the door opened.

The vacuum pump shown behind the receiver is of the vertical double-acting slide valve type, fitted with a special form of slide valve with transfer ports, designed to empty the clearance space at the end of the compression stroke into the suction side of the machine just after this has been closed from the vacuum space. In this way the volumetric capacity of the air pump is very materially increased, particularly at the higher vacuums, and it is also possible to provide a higher vacuum by this means.

Illustration (Fig. 20) shows the method of filling vacuum drying stove. The man is seen proceeding to place the trays containing the material to be dried into place. These trays—which can be of black steel, tinned iron, copper, aluminium, etc.—are arranged to come either directly on to the steam-heated surface, or in other cases are carried on runners clear of the surface. Usually a double set of trays are in use, one in the stove while the other is being discharged of the dry product and refilled with the wet material.

Illustration (Fig. 19) shows the double receivers, condenser and vacuum pump for vacuum drying stove.

This digression into the lay-out of a modern colour works, and the methods in vogue for the production of the prepared and dried pigments, will enable the manufacture of the various chrome yellows, so largely in demand at the present time, to be better understood.

The chrome yellows may appropriately be considered under the following shades, examples of the production of which will be given :—

- | | |
|---------------------|-------------------|
| 1. Primrose chrome. | 3. Middle chrome. |
| 2. Lemon chrome. | 4. Orange chrome. |

Chrome red (Persian red, Derby red, etc.) will also be, for convenience, considered in this chapter, as it is a basic chromate of lead and naturally falls under this group.

The chromes come on to the market as pure chromes and also as genuine chromes. They are also sold as reduced chromes Nos. 1, 2 and 3, the reduction in this case being obtained by the addition of terra alba. The genuine chromes are pure chromes to which a percentage (about 30 per cent.) of lead bottoms (sulphate of lead, PbSO_4) has been added.

1. PRIMROSE CHROME

This is the palest chrome on the market, and to obtain this exquisite delicate shade special care must be taken, as will now be described.

If a dilute solution of lead nitrate is run into a dilute solution of potassium chromate or bichromate, according to the equivalent proportions calculated from the equation given above, a pale yellow precipitate is formed. On washing and drying out this precipitate, however, a deep shade of chrome yellow is obtained—due to the instability and liability to change colour of the chrome so produced. To overcome this lack of stability it has been found by experience that the palest chromes can only be obtained under the following conditions :—(1) The reacting solutions must be very dilute. (2) The temperature must not rise above 80°F . during the whole of the reaction. (3) An excess of soluble neutral or acid lead salt must be present. (4) The chrome must be precipitated in conjunction with sulphate of lead whereby a sulpho-chromate of lead is formed, which has much more stability and permanency as regards change compared with the normal lead chromate.

The following examples will illustrate the method and proportions to be used so as to produce chromes of a delicate primrose shade :—

<i>Process A.</i>		<i>Process B.</i>	
Bichromate of soda	74 lbs.	Bichromate of soda	100 lbs.
Alum	112 „	Soda ash	31 „
Glauber salts	112 „	Glauber salts	80 „
Common salt	56 „	Salt	10 „
Lead nitrate	350 „	Lead nitrate	340 „
<hr/>		<hr/>	
Yield	276 „	Yield	240 „

Process A.—Dissolve the bichromate of soda (or potash) in the dissolving vat in about fifty times its weight of water; add the alum and stir occasionally till all is dissolved. If hot water is used the solution must be allowed to cool down to 75° – 80°F . The Glauber salt and common salt are next dissolved in another dissolving vat in about fifty times their weight of cold water.

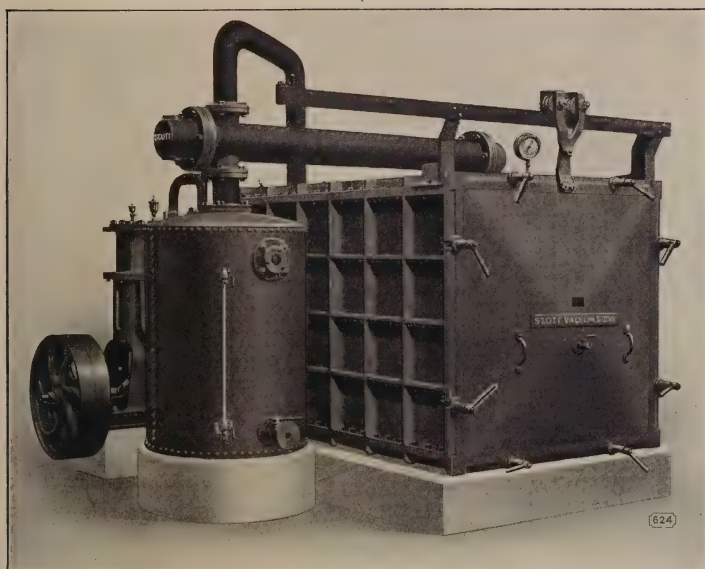
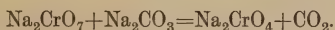


FIG. 18.—VACUUM DRYING STOVE. (George Scott & Son, Ltd.)

The nitrate of lead is dissolved in the precipitating vat in fifty times its weight of cold water. The stirrers are now set going in the large precipitating vat, and the contents of the two dissolving vats slowly run in, with constant stirring. A precipitate of primrose chrome is formed. After all the contents of the dissolving tubs have been emptied and washed out stirring is stopped, and the precipitate of primrose chrome allowed to settle down. After complete settlement (about twelve hours) the mother liquor is run off by knocking out the plugs in the side of the vat as low down as possible without disturbing the chrome. The large vat is then filled up with cold water, stirred well, and allowed to settle down.

The pale yellow precipitate is washed three or four times by decantation, till neutral, and then pumped out through the filter press, and dried at a low temperature.

Process B.—In process B the soda ash is dissolved in the bichromate solution. Effervescence takes place owing to the evolution of carbon dioxide and the bichromate is converted into the normal chromate according to the following equation :—



The process is otherwise carried out as in Example A.

Genuine Primrose Chrome and Reduced Chromes.—If a genuine primrose chrome is required then all that is necessary is to add the required amount of precipitated pulp sulphate of lead or lead bottoms (see Chapter VI.), to the precipitated chrome just after it has been struck.

This addition of sulphate of lead is also often done in the dry way; that is, the dried chrome is runnered in an edge runner or chaser (see Fig. 3) with the required amount of sulphate of lead until completely incorporated. The reduced grades of the chrome are obtained by adding the various amounts of terra alba (Paris white cannot be used as it tends to redden the shade of the chrome) according to the quantity required in Nos. 1, 2 or 3 chrome.

Pure primrose chrome is naturally one of the weakest of the chromes on account of the large amount of precipitated sulphate of lead that it contains.

2. PURE LEMON CHROME

This shade of chrome is produced in the cold in precisely the same manner as described under primrose chrome, the only difference being that the salt is omitted, and the proportion of alum and Glauber salts very considerably reduced. In this way the proportion of the normal chromate of lead to the alumina and sulphate of lead is very considerably increased. The alum also may be left out and its place taken by its equivalent of Glauber salts. This is usually done, as the Glauber salts are considerably cheaper than alum. On the other hand, the presence of a small proportion of alumina in a chrome has a very beneficial effect, tending to give softer and brighter tones.

The proportions given in the following examples will give a general indication as to how the lemon chromes are best produced.

<i>Examples—</i>	<i>A.</i>		<i>B.</i>	
Bichromate of soda or potash .	112 lbs.		Bichromate soda .	100 lbs.
Glauber salts	56 „		Soda ash	31 „
Alum	28 „		Glauber salts	60 „
Lead nitrate or acetate . . .	336 „		Lead nitrate	300 „
	<hr/>			<hr/>
Yield	276 „		Yield	210 „

As a general rule the bichromate of soda is always used in preference to bichromate of potash on account of the latter salt being more expensive.

The manufacturer in the case of lemon chrome has the choice of using either the acetate or nitrate of lead, according to which is more convenient.

It must, of course, be understood that each manufacturer has his own particular formula for producing the various chromes which give him the particular shade he requires, and which is the result of a long series of experiments and practical observations, taking into account such factors as dilution, temperature, rate of precipitation, and so on.

The examples given above are only to be taken as types which may be modified very considerably, always, of course, remembering that to produce yellow shades of chromes it is necessary to have excess of lead salts, and also that the sulphate of lead must be precipitated along with the chrome so that the stable sulpho-chromate is produced. In addition to this, in order to get the brightest and palest shades, it is necessary to work with cold dilute solutions.

Genuine Lemon Chrome and Reduced Lemon Chrome.—These chromes are obtained, as in the case of the genuine primrose chromes, by the mechanical addition of lead sulphate, or in the case of the Nos. 1, 2 and 3 lemon chromes by the addition of terra alba.

3. PURE MIDDLE CHROMES

Pure middle chrome is practically pure normal chromate of lead, only a small proportion of sulphate of lead being precipitated along with the chrome. On this account it possesses by far away the greatest body and covering power of all the chromes.

In the manufacture of this chrome the solutions used are considerably stronger (1·20) than in the case of the paler chromes; also the temperature of precipitation is about 200 F.

The proportion given in the following examples will show the method in use for the manufacture of this chrome.

<i>Examples—</i>	<i>A.</i>		<i>B.</i>	
Bichromate of soda	60 lbs.		Bichromate soda	100 lbs.
Glauber salts	10 „		Alum	10 „
Lead acetate	85 „		Lead nitrate	110 „
	<hr/>		Pulp white lead	100 „
Strike at about 200° F. yield . . .	55 „		Yield	120 „

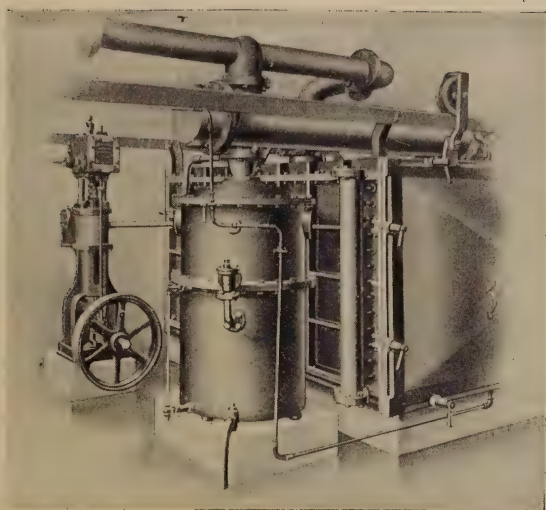


FIG. 19.—VACUUM DRYING STOVE SHOWING THE DOUBLE RECEIVERS, CONDENSERS AND VACUUM PUMP.

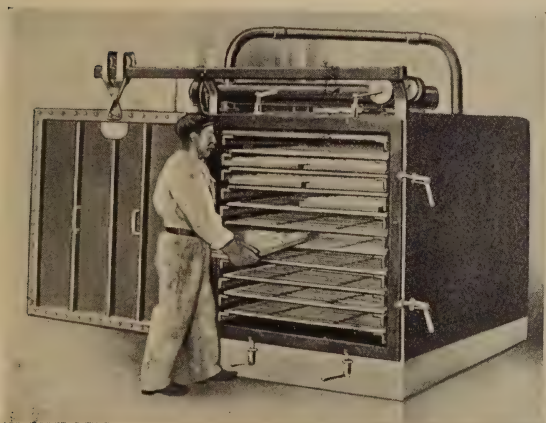


FIG. 20.—ILLUSTRATION SHOWING METHOD OF FILLING VACUUM DRYING STOVE.

In Example B the white lead pulp is mixed in the precipitation vat with the hot solution of the lead nitrate, and the hot bichrome run in, stirring well.

Genuine Middle Chrome and Reduced Middle Chromes.—Genuine middle chrome is produced by the addition of sulphate of lead to the pure middle as in the case of the primrose and the lemon chromes.

Sometimes white lead is present, due to the fact that an excess of white lead is used in its manufacture, and a certain proportion remains over unchanged.

The reduced grades contain terra alba in varying amounts.

4. PURE ORANGE CHROME

Orange chrome is a basic chromate of lead ($\text{PbCrO}_4\text{Pb}(\text{OH})_2$), associated with a certain proportion of the normal chromate of lead.

The formation of this pigment may be divided into stages. In the first stage, the normal chromate of lead (PbCrO_4) is formed; the second stage consists in boiling this with an alkali such as caustic soda or lime, by means of which part of the normal chromate is converted into a basic chromate of lead according to the equation (a) and (b) given at the commencement of this section (page 65).

On the manufacturing scale a solution of lead nitrate, or basic sugar of lead (obtained by dissolving litharge in a hot solution of lead acetate), is run into the hot solution of sodium bichromate or vice versa. Steam is passed through and the whole mass boiled and stirred for two or three hours, with the addition of a small quantity of milk of lime or caustic soda to produce the desired shade.

Test samples are drawn off from time to time and dried out, and when the right shade is obtained the boiling is stopped. After settlement the mother liquor is drawn off and the chrome well washed to remove all excess of alkali and soluble salts. If this is not carefully done the chrome will spot or blur when made up into a paint with oil. The chrome is then filter-pressed and dried.

The examples given below will illustrate the proportions used in the manufacturing scale:—

A. (Pale Orange).

Soda dichromate . .	100 lbs.
Lead nitrate . . .	150 „
Pulp lead	100 „
Caustic soda . . .	28 „

Yield 160 „

B. (Deep Orange).

Soda dichromate . .	100 lbs.
Basic sugar of lead . .	150 „
Lime	28 „

Yield 76 „

Properties.—The orange chromes vary in shade from a pale orange to an extra deep orange; they are soft in texture and have excellent body and covering power.

Genuine Orange Chrome is produced by adding red lead to the pure orange chrome; the reduced varieties contain terra alba, barytes, etc.

5. PURE CHROME RED (PERSIAN RED, DERBY RED, CHINESE RED)

This pigment, although a red pigment, is practically a pure basic chromate of lead ($\text{PbCrO}_4\text{Pb(OH)}_2$) and may therefore be conveniently described here.

It is a bright brick-red powder of a somewhat crystalline nature, this being especially noticeable in the deepest shades.

It is interesting to observe that if a portion be vigorously ground in a mortar so that it loses its crystalline nature, the colour will be found to have changed to an orange shade.

This red is now gradually falling into disuse and is not to-day manufactured to anything like the same extent as it used to be owing to its replacement by substitutes. These latter consist chiefly of red synthetic dye-stuffs struck on orange lead and barytes.

Manufacture.—The best shades of Persian red are obtained by boiling over a direct fire a strong solution of bichromate of potash and pulp white lead, with the addition of a small amount of caustic soda.

The reaction takes place according to the following equations :—



<i>Example 1.</i> Bichromate of potash	.	.	.	100 lbs.
Pulp lead	.	.	.	500 „
60 per cent. caustic soda	.	.	.	15 „

Properties of Lead Chromes.—The properties of the lead chromes naturally varies enormously according to their colour, but in general they may be regarded as pigments possessing remarkably good body and exceptional brightness of tone. They have an extremely soft texture, with the exception of Persian red, which is apt to be coarse on account of its crystalline nature.

The lemon chromes are readily affected by alkalies, turning to orange or chrome red ; for this reason they cannot be used for distempers or lime colours.

On exposure of hydrogen sulphide they darken owing to the formation of black sulphide of lead.

The chromes are all completely soluble in a dilute solution of nitric acid, which affords a ready means of testing their purity, any adulteration such as barytes, gypsum, lead sulphate bottoms being left behind as an insoluble residue.

When ignited the chromes turn dark brown with the evolution of oxygen and leave behind a residue of oxides of lead and chromium.

The strength of a chrome is best determined by adding to it a definite amount of Chinese blue and comparing the green shade produced against the standard chrome similarly treated. By this means the cleanness of a chrome (also a blue if a standard chrome is taken) may be readily seen.

Specification.—The general specification required of a chrome is as follows :—

1. The chrome must contain 98 per cent. of lead compounds and be free from all added material such as lead sulphate bottoms, barytes, terra alba, and so on.

2. It must be fine in texture, free from all coarse particles, and equal in shade to the approved standard.

3. On reduction with ten times its weight of zinc oxide in linseed oil the resultant shade must be equal to the standard similarly reduced (strength test).

4. It must contain less than 0.5 per cent. of moisture and not more than 2 per cent. of water soluble matter.

Method of Analysis.—The general scheme used in the analysis of the lead chromes will be now briefly outlined. It must be, however, first mentioned that it is always advisable to conduct a quick preliminary qualitative analysis as much subsequent labour will in many cases be saved thereby.

1. *Moisture.*—Heat 5 gms. at 100° C. till constant.

2. *Insoluble.*—Barytes (occasionally silica or China clay). Boil 1 gm. of pigment for half an hour with 50 c.c. concentrated hydrochloric acid, adding a little reducing agent, such as alcohol. Filter, wash thoroughly, ignite, and weigh.

Note.—If lead bottoms are present in the chrome, as they frequently are, prolonged boiling is necessary to ensure that they are completely dissolved, inasmuch as this body is very much more insoluble than the sulphate of lead, which is directly precipitated along with the chrome.

3. *Lead.*—The filtrate from the insoluble is evaporated to dryness to remove the excess of acid, then taken up with a few drops of hydrochloric acid and diluted with 250 c.c. of hot distilled water. Hydrogen sulphide is passed through till the solution is saturated and all the lead is precipitated. Filter, wash, and dissolve the precipitate in dilute nitric acid. Precipitate and weigh as sulphate of lead.

4. *Chromium.*—The filtrate from the lead sulphide is boiled to remove all hydrogen sulphide; then made alkaline with ammonia. The precipitate of chromium and aluminium is treated with a hot solution of sodium peroxide till dissolved; it is then made up to 250 c.c. 50 c.c. are filtered out, acidified with acetic acid, and excess of lead nitrate solution added.

Filter off, wash, dry, and weigh as PbCrO_4 .

5. *Aluminium.*—Take 100 c.c. of the 250 c.c. solution and acidify with hydrochloric acid. Re-precipitate with ammonia, wash and ignite, and weigh as Al_2O_3 .

6. *Calcium.*—To the filtrate from the iron and alumina add ammonia and ammonium oxalate. Ignite precipitate=calcium oxide (CaO).

7. *Sulphates.*—Dissolve 2 gms. of the chrome in hydrochloric acid, filter off insoluble and precipitate hot in dilute solution with barium chloride. Weigh as barium sulphate.

Or the lead may first be removed by precipitation with aluminium and then the barium chloride added to precipitate the sulphate.

8. *Carbonates.*—Estimate in the Schrötter apparatus in the usual way.

The following analysis by the author of the various pure chromes will give the reader a clear idea as to their composition :—

Result of the Analyses of Pure Chromes

<i>Pure Primrose.</i>			<i>Pure Lemon.</i>		
Lead sulphate	.	26.70 per cent.	Lead sulphate	.	19.20 per cent.
Lead chromate	.	68.35 "	Lead chromate	.	76.50 "
Alumina	.	3.55 "	Alumina	.	2.90 "
		<hr/> 98.60 "			<hr/> 98.60 "
<i>Pure Middle.</i>			<i>Pure Orange.</i>		
Lead sulphate	.	trace	Lead chromate	.	79.90 per cent.
Lead chromate	.	90.50 per cent.	Lead carbonate	.	18.70 "
Lead carbonate	.	7.49 "			<hr/> 98.60 "
		<hr/> 97.99 "			
<i>Pure Persian Red.</i>					
Lead oxide	.	78.30 per cent.			
Chromic oxide	.	17.80 "			
		<hr/> 96.10 "			

Analyses of Genuine Chromes

<i>Genuine Lemon Chrome.</i>			<i>Genuine Orange Chrome.</i>		
Lead sulphate	.	35.50 per cent.	Lead chromate	.	72.00 per cent.
Lead chromate	.	64.00 "	Lead carbonate	.	7.25 "
Alumina, etc.	.	0.50 "	Red lead	.	20.50 "
		<hr/> 100.00 "			<hr/> 99.75 "

Analyses of Reduced Chromes

<i>No. 3 Lemon Chrome.</i>			<i>No. 1 Middle Chrome.</i>		
Lead sulphate	.	15.50 per cent.	Lead chromate	.	45.50 per cent.
Lead chromate	.	22.65 "	Lead carbonate	.	4.90 "
Calcium sulphate	.	62.75 "	Barytes	.	49.42 "
		<hr/> 100.90 "			<hr/> 99.82 "

No. 3 Chinese Red

Lead chromate	.	15.50 per cent.
Red lead (Pb_3O_4)	.	50.20 "
Barytes	.	30.55 "
		<hr/> 96.25 "

This sample contained a dye-stuff soluble in alcohol.

ZINC CHROME

(Zinc Yellow, Zinkgelb, Jaune de Zinc.)

Zinc chrome consists essentially of zinc chromate (ZnCrO_4), but on analysis it is found that there is always associated with it a certain proportion of potassium bichromate and also zinc oxide.

Manufacture.—In the manufacture of zinc chrome it is essential that only the best grades of zinc oxide are used, such as the “Snow White” brands. The presence of any lead or iron in the zinc oxide is very objectionable in the preparation of a first-class product. On the manufacturing scale the process used is as follows :—

The zinc oxide is pulped up in water on flat stones so as to get it into a very fine state of sub-division ; it is then transferred to the precipitating vat and mixed up with cold water to a thin cream. The requisite amount of concentrated sulphuric acid (C.O.V.) is next cautiously added whilst stirring so as to convert a proportion of the zinc oxide into sulphate of zinc.

After stirring for one hour a hot bichromate of potash solution is next run in from the dissolving tubs. The precipitated zinc yellow thus formed is allowed to settle and the top liquor, which always contains excess of potassium bichromate in solution, is run off.

As the zinc chrome is rather soluble only one wash is given before filter-pressing and drying.

The best temperature of precipitation is about 120°F . If the temperature gets too high or too low a very coarse crystalline product is produced, which is useless as a pigment.

The following example will illustrate the proportions which may be used to produce a good bright shade of zinc chrome.

<i>Example</i> —Zinc oxide	100 lbs.
Potassium bichromate	125 „
Sulphuric acid conc.	36 „
						<hr/>
Yield	<u>175 „</u>

Properties.—Zinc chrome is a yellow pigment having a bright clean pale shade. It is readily soluble in all mineral acids, also (unlike lead chrome) in warm dilute acetic acid.

On heating it changes to a dark purple tint due to its decomposition to zinc oxide and chromium oxide. It is not affected by lime or sulphuretted hydrogen ; hence it is largely used for the production of lime yellows for tinting distempers. Zinc chrome is unfortunately lacking in body and strength as compared with chrome yellow.

In conjunction with Chinese blue we get the useful non-poisonous range of zinc greens which are finding increasing favour in the paint trade.

Specification.—The general specification required for zinc chrome is as follows :—

The zinc chrome must be of a soft texture and equal in colour to the standard shade.

It must be free from any lead compounds or aniline dyes, or any added matter whatever such as zinc oxide, whiting, barytes, etc., and should be completely soluble in a hot dilute solution of acetic acid. On reducing with ten parts of zinc oxide in linseed oil the resultant shade must be equal to the standard sample reduced to a similar extent.

An Analysis of a Pure Zinc Chrome

Zinc oxide	15.50 per cent.
Zinc chromate	64.25 „
Soluble matter (by difference)	20.25 „
	<hr/>
	100.00 „

Method of Analysis

(A) Gravimetric. Dissolve $\frac{1}{2}$ gm. of the zinc chrome in dilute hydrochloric acid. Should there be any insoluble this must be filtered off, dried, and weighed = barytes or silica. Add 250 c.c. distilled water and about 2 gms. of ammonium chloride. Boil and precipitate with excess of ammonia. Filter and wash well. Ignite and weigh as Cr_2O_3 .

Zinc.—Add colourless ammonium sulphide to the filtrate from the chromium. Boil well to coagulate the precipitate (zinc sulphide). Filter and wash.

Then dissolve the zinc sulphide thus obtained in dilute hydrochloric acid. Boil to remove all sulphuretted hydrogen, and precipitate with anhydrous soda carbonate. Filter and wash.

Ignite the zinc carbonate precipitate to zinc oxide and weigh.

Volumetric Estimation.—The amount of zinc chromate may be volumetrically estimated as follows :—

Weigh out $\frac{1}{2}$ gm. Add 50 c.c. (or 100 c.c. if necessary) of ferrous sulphate solution (30 gms. FeSO_4 to 1 litre water). Titrate with standard bichrome solution (10 gms. to 1 litre water), using potassium ferricyanide as outside indicator.

Example—

50 c.c. FeSO_4 = 26.1 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

$\frac{1}{2}$ gm. ZnCrO_4 requires 100 c.c. FeSO_4 solution from pipette.

2 \times 50 c.c. FeSO_4 solution = 52.2 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

Amount of $\text{K}_2\text{Cr}_2\text{O}_7$ required for excess FeSO_4 = 26.5 c.c.

52.2 c.c. — 26.5 c.c. = 25.7 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$.

1 gm. $\text{K}_2\text{Cr}_2\text{O}_7$ = 1.227 ZnCrO_4 .

1 c.c. $\text{K}_2\text{Cr}_2\text{O}_7$ = .01 gm. $\text{K}_2\text{Cr}_2\text{O}_7$.

Therefore ZnCrO_4 = 64 per cent.

Note.—This method is also applicable for the volumetric estimation of lead chromate. 1 gm. $\text{K}_2\text{Cr}_2\text{O}_7$ = 2.196 gms. PbCrO_4 .

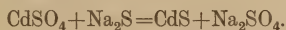
We have now described the preparation and properties of the most important inorganic yellow pigments in general use. (For a description of the yellow lake colours see Chapter XIII. on Lakes).

There are also a number of other yellow pigments which are known and have a limited use for particular purposes, but for a detailed description of these the reader is referred to the various reference books which deal exclusively with this subject. Mention, however, may be made of the following:—

Barium Chrome or Barium Chromate (BaCrO_4).—This is made by adding a solution of barium chloride to a solution of sodium bichromate. This pigment has a pale yellow colour, and lacks body. It is used to a small extent by paper stainers.

Naples Yellow (Jaune de Naples).—Naples yellow is a compound of the oxides of antimony and lead, and always contains an excess of lead oxide. There are various shades of this yellow according to the particular method of its preparation. It is chiefly used in oil by artists.

Cadmium Yellow (CdS).—This pigment is a sulphide of cadmium, and is mainly used by artists. The shades vary from yellow to orange. The following equation represents its method of formation:—



King's Yellow (As_2S_3) (*Königs Gelb*).—This pigment is a sulphide of arsenic. It occurs in nature as the mineral orpiment.

Realgar (*Arsenic Orange*) (As_2S_2) is a disulphide of arsenic and occurs native as realgar. It has a pale orange-red colour, and has been used as a pigment by artists.

Cassel Yellow is an oxychloride of lead of the composition $\text{PbCl}_2 \cdot 7\text{H}_2\text{O}$, obtained by heating lead oxide and ammonium chloride. It is no longer used as a pigment.

Aureolin (*Cobalt Yellow*).—This yellow pigment was discovered by Fischer. It is a compound of the nitrates of cobalt and potassium represented by the formula $\text{K}_3\text{Co}(\text{NO}_2)_6$. This pigment has a fine transparent yellow, but is only moderately permanent.

It has been used to a limited extent as an artists' colour. It is prepared by mixing an acid solution of a cobaltous salt with a concentrated solution of potassium nitrate.

Indian Yellow (*Purree, Puri*).—This interesting and curious yellow pigment is an organic body, but may be mentioned here briefly for the sake of convenience.

It is an impure magnesium salt of euxanthic acid ($\text{C}_{19}\text{H}_{16}\text{O}_{11}\text{Mg}$, $5\text{H}_2\text{O}$), and is made at Monghyr, a town in Bengal, from the urine of cows which have been fed on mango leaves.

The fresh urine, of a bright yellow colour, is boiled down in earthenware vessels, and the yellow deposit thus formed is collected on calico, made into balls, and sold in the bazaars.

Pure Indian yellow has a deep transparent yellow colour of considerable beauty. It is used as a water and oil colour by artists, but is only moderately permanent.

CHAPTER VIII

THE BLUE PIGMENTS

THE ultramarine blues and the Prussian blues are by far away the most important blue pigments, and those in most extensive use at the present time. The remaining known blue pigments, such as the various copper and cobalt blues that have been introduced from time to time, have all been gradually superseded by one or other of them, and at the present time they do not come on to the market in any quantity, and their use is now very limited.

ULTRAMARINE BLUE

(Ultra Blue)

This pigment is by far the most important of the blue colours.

Historical.—Ultramarine occurs in nature as lapis lazuli, a beautiful, blue-coloured crystalline mineral found in Siberia, Persia, Thibet, and China. Analysis shows it to be a silicate of aluminium and soda, with some combined sulphur.

It was largely used by artists in the Middle Ages, who prepared it for use by repeatedly grinding the mineral in water to an extreme state of fineness and washing through fine strainers.

Owing to the scarcity of the mineral lapis lazuli, and to the elaborate and tedious method of its preparation, genuine ultramarine was extremely costly. On this account endeavours were made to produce it artificially, and so successful have these been, that at the present time the whole of the ultramarine used in commerce is made artificially.

Guimet of Toulouse, the eminent French manufacturing chemist, studied the production of ultramarine, stimulated by the offer of a prize of 6000 francs by the Société d'Encouragement de France in 1824 to anyone who should succeed in manufacturing ultramarine artificially at a cost not exceeding 300 francs per kilogramme. He was awarded the prize in 1828, being the first to devise a suitable process for its manufacture.

Christian Gmelin of Tübingen about the same time published a full description of his method of making it.

Kottig also perfected a process for the production of artificial ultramarine at the Royal Porcelain Works at Meissen in about 1828, and this works was for many years one of the leading producers of this material.

The great bulk of the material on the market at the present time comes from Germany and France. There are, however, a few works in England, Belgium, and the United States.

The Manufacture of Ultramarine.—At the present time the manufacture of ultramarine is carried out, as a rule, by firms which are engaged exclusively in the production of this material; in other words, it is a special industry. The reason for this is that not only are the technical difficulties to be overcome very great, but a vast amount of experience is necessary in order to produce high-class grades; in addition a special and very expensive plant is required.

A brief account of the manufacture of this blue, according to the most modern methods, will now be given. The reader who wishes an exhaustive account is referred to those books dealing exclusively with the subject (see Bibliography).

The artificial ultramarines that come into the market may be divided into three varieties as follows:—

1. *Sulphate Ultramarine*, which is a pale greenish blue colour. It possesses little covering power, and is readily acted on by a solution of alum.

2. *Soda Ultramarine A* (containing only a little sulphur), which is a dark blue colour. It has more covering power than the sulphate ultramarine, but is not so readily acted on by alum solutions.

3. *Soda Ultramarine B* (containing a high percentage of sulphur), which is a very dark blue colour with a reddish tinge. It also contains a higher percentage of silica than the (*A*) variety, which makes it very resistant to alum solutions; hence it is largely used in the paper trades.

The raw materials used in the manufacture of ultramarine are:—

- (1) China clay (kaolin).
- (2) Soda ash.
- (3) Anhydrous sodium sulphate.
- (4) Sulphur.
- (5) Coal, charcoal, rosin, pitch, etc.
- (6) Kieselguhr, silica, quartz, etc.

The manufacture of the ultramarine may be divided into the following operations:—

- (1) The mixing and grinding of the raw materials.
- (2) Calcining the finely-ground material. (This gives green ultramarine.)
- (3) Grinding the green ultramarine to an impalpable powder.
- (4) Blueing the green ultramarine by roasting.
- (5) Finishing ultramarine.

1. THE MIXING AND GRINDING OF THE RAW MATERIALS

For the production of ultramarine it is essential that the mixed raw materials should be ground to a very fine state of subdivision. This is done in powerful edge runners or in ball mills.

The mixings in general use for the manufacture of the above-mentioned three varieties are roughly as follows, though of course each manufacturer has his own particular proportions which he has found by experience gives him the best results, and which he carefully guards as a trade secret :—

<i>Raw Materials Mixture.</i>	<i>Sulphate Ultramarine.</i>	<i>Soda Ultramarine.</i>	
		A.	B.
China clay	100	100	100
Anhydrous soda sulphate	150
Soda ash	150	150
Coal	50	30	10
Silica	5	20
Sulphur	25	75	125

2. CALCINING THE FINELY-GROUND RAW MATERIAL. GREEN ULTRAMARINE

The finely ground material is packed tightly into a large number of fire-clay crucibles, which are fitted with lids so as to exclude the air. The crucibles are put into a large muffle furnace in rows, and packed one on the other till the oven is full.

The furnace is then bricked up and heated slowly to a white heat and maintained at this temperature for about eight hours. The fires are then drawn and the oven slowly allowed to cool down. This takes about two days, and care must be taken that the cooling down is gradual, otherwise the final product will be spoiled.

The furnaces are built in series, so that as one is cooling down the other can be charged.

3. GRINDING THE GREEN ULTRAMARINE

The contents of the crucible, when cold, are emptied out into large ball mills, and finely ground.

Formerly it was customary to grind the green ultramarine under water, and wash out the soluble soda salts present, then dry and powder again. But this process, on account of its cost, has been superseded by the dry grinding process without any detriment to the finished product.

4. "BLUEING" PROCESS

The powdered green ultramarine is next converted into blue ultramarine by the addition of sulphur and heating in a furnace at a low temperature.

There are many ways of carrying out this operation and each country has its own peculiar method. The simplest method consists in spreading the green ultramarine on the floor of a kind of modified reverberatory furnace. The fire is lighted and when the temperature is high enough to ignite sulphur, a quantity of this material is thrown on and well stirred up. When this sulphur has burnt out more is added, and so on till the whole of the green ultramarine has been converted into the desired blue shade. The blue mass of crude ultramarine is then raked out.

5. FINISHING ULTRAMARINE

The coarse blue particles from the furnaces contain a considerable amount of Glauber salts, and before this crude ultramarine can be used as a pigment it is necessary to remove these salts, and, at the same time, to grind the crude material to an extreme degree of fineness.

The usual method now in use is to lixiviate the crude material with boiling water in order to remove all soluble salts which are present, and then to grind this washed ultramarine blue between flat stones till the colour is fully developed and the required degree of fineness obtained. The ground material is then levigated, and the pasty mass spread on long drying hearths heated by waste heat from the furnaces.

The dried ultramarine comes from the hearths in the form of large cakes or lumps, and is emptied into a ball mill where it is re-ground to the required degree of fineness. It is then sifted through 80–120 inch. sieves and is ready for use.

PROPERTIES AND USES OF ULTRAMARINE

Ultramarine on account of its beautiful blue colour and permanency has come to be very largely used in many industries at the present time. It is extensively employed in the paint industry both as an oil paint, tinter, and whitener; also in lime washes and distemper paints owing to its valuable property of being unaffected by lime or alkalies.

It is also largely used for the “blueing” of whites or yellowish white materials such as barytes, white paints, paper pulp, starch, zinc oxide, sugar, etc., whereby the resulting whiteness of the colour appears to the eye to be very considerably enhanced.

Ultramarine is unaffected by heat. Although unaffected by alkalies it is readily acted on by even dilute acids. A characteristic test of ultramarine consists in heating a portion with a dilute acid; the colour is at once discharged, sulphuretted hydrogen is evolved, and silica and sulphur are thrown down.

Ultramarine is rather a transparent colour and somewhat lacking in body. When grinding to a stiff paste in oil there is always an unpleasant sulphur odour noticeable, which is characteristic of this pigment, and is due to the heat of the grinding operation causing an action between the sulphur and the oil used.

Hot alum solutions tend to destroy the colour of the sulphate ultramarines, and on this account paper-makers choose the soda ultramarine, variety B (which contains a large amount of silica and sulphur), because of its more resistant properties.

The cobalt shade ultramarine blue obtained by the action of ammonium chloride on ultramarine is in moderate request owing to the beauty and cleanness of its shade.

Besides ultramarine blue other varieties are also known, such as the violet, red, and yellow ultramarines; but as these are practically never met with in commerce it is unnecessary to describe them.

CONSTITUTION OF ULTRAMARINE

Ultramarine is a compound of silica, containing alumina, soda, sulphur, and combined sulphuric acid.

The constitution of ultramarine is exceedingly complex, and many chemists have at different periods undertaken investigations with a view to elucidating the problem of its composition without, however, much success; due mainly to the many varieties there are according to the methods and proportions used in manufacture.

Hoffmann considered ultramarine to be a double silicate of alumina and soda, combined with bisulphide of sodium according to the following formula: $2(\text{Al}_2\text{Na}_2\text{Si}_3\text{O}_{10})\text{Na}_2\text{S}_4$.

ANALYSIS OF ULTRAMARINES

Moisture.—Heat 5 gms. in water oven till constant.

Insoluble (Silica).—Dissolve 1 gm. in 50 c.c. concentrated hydrochloric acid. Take to dryness and bake on the hot plate to render all the silica insoluble.

Take up with 10 c.c. hydrochloric acid and 100 c.c. hot water. Filter, ignite, and weigh as silica (SiO_2).

Test with platinum wire to make sure that no barytes is present. This is unlikely, as the adulterants added are as a rule terra alba, Paris white, or silica.

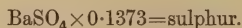
Alumina (Al_2O_3).—Take filtrate from silica, warm up, and add ammonia in excess. This precipitates the alumina.

Filter, wash and ignite, and weigh as alumina.

Sodium Oxide (Na_2O).—The filtrate from the alumina is neutralised with sulphuric acid, evaporated to dryness and ignited till all ammoniacal fumes have been given off, cooled and weighed=sodium sulphate. To convert to sodium oxide multiply by 0.4366.

Total Sulphur.—Fuse 1 gm. with a mixture of potassium nitrate and potassium chlorate for about one hour. Dissolve the fused mass in hot water with the addition of concentrated nitric acid. Filter off the insoluble silica and add barium chloride to filtrate.

Filter, wash well, ignite and weigh=barium sulphate



From this weight deduct the weight of sulphur present as combined sulphuric acid to find the quantity of sulphur actually present as sulphide.

Combined Sulphuric Acid.—Weigh 2 gms. ultramarine blue; treat with dilute hydrochloric acid, filter, precipitate with barium chloride; again filter, wash, ignite, and weigh as barium sulphate BaSO_4 . $\text{BaSO}_4 \times 0.3422 = \text{sulphur trioxide } (\text{SO}_3)$.

ANALYSES OF ULTRAMARINE BLUES BY THE AUTHOR

The results of the following analyses which are here given were made by the author on ultramarine blues that were being employed in the manufacture of paint and for tinting purposes.

	1	2	3
Moisture	0.25	.31	.12
Silica	41.50	38.00	14.50
Alumina	26.00	25.40	9.60
Sulphur	11.55	9.78	3.62
Sulphur trioxide	2.50	3.25	1.20
Sodium oxide	18.20	23.26	9.40
Calcium sulphate	61.56
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Note.—No. 3 was an ultramarine reduced with terra alba, known in the trade as lime blue.

LIME BLUE

Lime blue denoted originally a copper hydroxide mixed with calcium sulphate, and was obtained by adding milk of lime to sulphate of copper solution. This is now quite obsolete, and the only lime blues that come on to the market at the present day are :—

1. Ultramarine blues heavily reduced with terra alba (see analysis above), or
2. Aniline pigment colours, which are made by striking or precipitating a blue synthetic dye-stuff such as methylene, or similar blue dye-stuff, on to a suitable white base.

Lime Blues are very extensively used for adding to lime washes and for distemper colours.

PRUSSIAN BLUE

(Chinese Blue, Paris Blue, Berlin Blue, etc.)

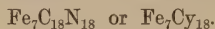
Introduction.—Prussian blue is one of the most valuable and widely used blue pigments at the disposal of the paint manufacturer.

Enormous quantities of this blue are used in the paint and printing ink trades on account of the beauty and brilliancy of its colour and shades. Moreover, in association with chrome yellow in varying proportions, we get a most extensive and variegated range of green pigments known as the Brunswick greens, which are extensively used at the present time.

Prussian blue was accidentally discovered about the year 1704 by Diesbach, a Berlin lake maker, who communicated his discovery to a French pupil of his named De Pierre, and who later started making this pigment in a small way in Paris. Hence the name Paris blue.

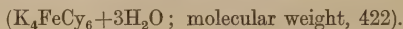
Wilkinson in London next commenced manufacturing the pigment, and gradually more and more colour firms took up its production, till at the present time many thousands of tons are produced yearly.

Composition.—Prussian blue is a compound of iron, carbon and nitrogen, the carbon and nitrogen being combined in a cyanide thus:—



On careful analysis it is found that true Prussian blues always contain potassium as an essential part of their composition, the formula of which may be represented as $\text{KFe}(\text{FeCy}_6)$.

Raw Material.—The chief raw material for the manufacture of Prussian blue is prussiate of potash or potassium ferrocyanide—

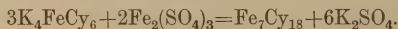


This salt comes on to the market in the form of large yellow tabular crystals, which are soft to the touch.

Potassium ferrocyanide or yellow prussiate of potash is manufactured by calcining caustic potash with charred nitrogenous substances such as scraps of horn, blood, hide, clippings, etc., in the presence of iron filings. The black fused mass, when the reaction is over, is lixiviated with boiling water and evaporated down; it is then run into pans and allowed to crystallise out.

At the present time a large amount of ferrocyanide is obtained from gas-works by-products. The spent gas lime resulting from the purification of the coal gas is treated with caustic lime, calcium ferrocyanide being formed. This is decomposed by potash and potassium chloride into potassium ferrocyanide. In many of the largest gas-works, however, these by-products are now worked up directly so as to produce Prussian blue, and very large amounts are turned out annually in this way.

Prussian blue is obtained as a deep blue precipitate when a solution of a ferric salt is added to a solution of potassium ferrocyanide. This reaction may be expressed according to the following simple equation:—



Potassium ferrocyanide + Ferric sulphate = Prussian blue + Potassium sulphate.

At this stage it will be convenient to consider the methods and processes in general use at the present time for the production of Prussian blues on the commercial scale.

THE MANUFACTURE OF PRUSSIAN BLUE

The manufacture of this colour on the large scale is attended with very considerable difficulties.

In the first place, very large vats are required, since it is necessary to work with dilute solutions in order to get the best qualities and shades. Moreover, this pigment, by reason of its extreme degree of fineness of precipitation and its bulkiness, takes a very long time to settle out.

This makes the washing and filtering operations very tedious and protracted,

and it will be readily seen that a large plant is necessary if the manufacturer is to produce any considerable quantity of these blues.

Prussian blue, as has already been pointed out, is produced by adding a solution of a ferric salt to a solution of prussiate of potash. As ferric salts are not readily available, it is cheaper and more usual for the manufacturer to use ferrous sulphate. This salt when added to prussiate of potash gives a whitish precipitate of ferrous ferrocyanide, which on oxidation is converted into Prussian blue.

RAW MATERIALS

Ferrous Sulphate ($\text{FeSO}_4 + 7\text{H}_2\text{O}$; molecular weight, 278).—This salt, commonly known as green copperas, is a pale bluish-green crystalline substance, which can be readily made by adding scrap iron to dilute sulphuric acid, thus—



The colour maker, however, hardly ever makes his own green copperas in this way, as he can buy it exceedingly cheaply owing to its being a by-product in various industries, e.g. it is obtained from the waste iron liquors of galvanising plants in large quantities, and is often sold to the blue manufacturer in the form of large cakes or slabs known as “slab” copperas.

Prussiate of Potash used to be made by the colour maker in the early days of the manufacture of Prussian blue, but nowadays this is never done as the saving is trifling, and a much purer and better product can be bought from those chemical works which make a speciality of this salt.

As will be readily understood, there are many methods in use for the manufacture of Prussian blue, and each manufacturer has his own particular process and methods of working. An attempt, however, will be made to give a brief description of the most important methods that are now in use for the preparation of this pigment.

The processes in use may for convenience be divided into two parts :—

- (1) The formation of the white precipitate of ferrous ferrocyanide.
- (2) Oxidation of ferrous ferrocyanide to ferric ferrocyanide or Prussian blue.

The variations in the different processes of manufacture mainly consist in the way in which the white precipitate of ferrous ferrocyanide is oxidised to Prussian blue. The manufacturer produces ferrocyanide blues of varying shades at will according to which process or processes of oxidation he makes use of, as described in the examples given below :—

PROCESS 1.—OXIDISING AGENT: BICHROMATE OF POTASH + SULPHURIC ACID

100 lbs. prussiate of potash are mixed in about 90 gals. of hot water in the dissolving vat (see Colour House Plant, Chapter VII.), and well stirred till all is dissolved.

90 lbs. of green copperas are next dissolved in about 90 gals. of hot water in another dissolving tub, well stirred until all is taken up, then 10 lbs. of concentrated sulphuric acid added to clear the solution (this converts any ferric iron into

the ferrous state). The green copperas solution is then run down into the precipitating vat through the strainers, so as to remove any insoluble matter.

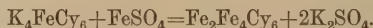
The stirrers in the lower or precipitating vat are set going, and the hot prussiate solution rapidly run in. A greenish-white precipitate of potassium ferrous ferrocyanide ($\text{KFe}_2\text{FeCy}_6$) is immediately formed.

This body is readily oxidised in the presence of air, as may be seen by the bluish shade that appears on the top of the vat. The oxidising agents are next immediately added, as it is most important in order to get clean bright blues that the oxidation should proceed very rapidly.

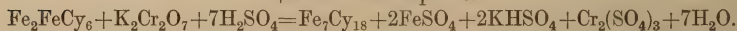
Practice has proved that the best and most convenient oxidiser—and which is the one now in general use—is a mixture of bichromate of potash and sulphuric acid.

On to the white precipitate obtained as above there is next poured in, with constant stirring, 48 lbs. of concentrated oil of vitriol, and then 16 lbs. of lump bichromate of potash is added. The white mass immediately turns blue owing to its oxidation to potassium ferric ferrocyanide or Prussian blue $\text{KFe}_2(\text{Fe}_2\text{Cy}_{12})$.

The reactions that take place may be simply expressed by the following equations :—



Potassium ferrocyanide + Ferrous sulphate = Ferrous ferrocyanide
+ Potassium sulphate.



Ferrous ferrocyanide + Potassium bichromate + Sulphuric acid = Prussian blue
+ Ferrous sulphate + Potassium hydrogen sulphate + Chromium sulphate + Water.

The temperature at which the whole reaction is carried out should be as high as possible, and if the solutions fall below 90°C . steam should be passed through so as to raise the temperature to near the boiling-point again.

The precipitate of Prussian blue thus obtained is in an extremely fine state of suspension, and must be left for about twenty-four hours to settle, for it settles very slowly.

The mother liquor is removed in the usual way by knocking out the plug holes in the sides of the vat one by one as the precipitate settles down.

The blue is then washed with cold water two or three times till quite free. A quick test to see if the blue is free is to take a drop of the waste liquor out and test with blue litmus. If neutral, then filter press, and dry out in the drying rooms at a moderate temperature.

PROCESS 2.—OXIDISING AGENT: BLEACHING POWDER

The proportions used and the method of preparing the whitish-green precipitate of potassium ferrous ferrocyanide are precisely the same as described under Process 1.

At this stage the method of procedure is as follows :—The whitish-green precipitate is well washed three times with cold water to remove all soluble salts, and then 30 lbs. of concentrated hydrochloric acid is added.

A solution of bleaching liquor is made up as follows :—50 lbs. fresh bleaching

powder are stirred into 25 gals. of water for four hours, and then left to settle overnight.

The clear liquor is then run into the thick white precipitate of potassium ferrous ferrocyanide (to which has already been added the concentrated hydrochloric acid) with constant stirring. By this means we get the whole of the white precipitate oxidised into the blue potassium ferric ferrocyanide.

The Prussian blue is then washed, filtered and dried.

Bronze Blue.—The blue obtained by this method has a beautiful reddish-bronze appearance, and is often on this account sold under the name of Bronze blue.

PROCESS 3.—OXIDISING AGENT: POTASSIUM CHLORATE AND HYDROCHLORIC ACID

The method is the same as described in Process 2, but in this case the washed potassium ferrous ferrocyanide (white precipitate) is treated as follows:—

The washed precipitate is well stirred and steam passed through to raise the temperature to about 180° F. Then 25 lbs. of concentrated hydrochloric acid are stirred in, and immediately afterwards a solution made up of 15 lbs. of potassium chlorate dissolved in 10 gals. of hot water run in.

The contents of the vat are stirred for three-quarters of an hour, then allowed to settle. The blue is next washed, pressed and dried.

Chinese Blue.—The blue made by this process is known as Chinese blue, a name which is given to the best qualities of Prussian blue. Although it has precisely the same composition as Prussian blue, its physical characteristics are different.

For example, Prussian blue is a dark reddish blue, with a red undertone, whereas Chinese blue is a much paler blue, and is characterised by having a pale violet shade with a green undertone.

Chinese blue is largely used by calico printers and dyers, and also in the manufacture of Brunswick greens and zinc greens.

Properties and Uses of Prussian Blue.—Prussian blue (also known as Paris blue and Berlin blue) possesses a characteristic dark blue colour, and is largely used in the paint and printing ink trades. It is a brittle substance and extremely hard to grind to a fine powder. Great care is required in grinding the material, as any overheating is apt to cause the blue to ignite.

The varieties known as Chinese blue, Milori blue and Steel blue are identical in composition with Prussian blue, but are considerably paler in shade.

Prussian blue by special methods of treatment can be produced possessing a very highly bronzed coppery lustre, which is much esteemed (see Process 2); such blues are known as Bronze blues.

Prussian blue is rather a transparent colour, and hence is deficient in covering power. It is fairly permanent to air and light; but when used for tinting pale shades in conjunction with chrome and zinc oxide or white lead the colour tends to fly. It is insoluble in water, but completely soluble in a 10 per cent. solution of oxalic acid.

Prussian blue is not acted on by dilute acids, but in the presence of weak alkalis is immediately decomposed into a ferrocyanide of the alkali and oxide of iron. On

the addition of excess of acid the blue colour is restored. On account of this action of alkalis in discharging the blue colour it is impossible to use Prussian blue in distempers or lime colours. This test affords a ready means of distinguishing Prussian blue from other blues.

On gentle ignition Prussian blue is decomposed, leaving a reddish-brown residue of ferric oxide, the cyanogen burning off to nitrogen and carbon dioxide.

Analysis of Prussian Blues.—The scheme for the analysis of Prussian blues is as follows :—

Moisture.—Weigh out 5 gms. and heat in water oven till constant.

Iron.—Ignite 1 gm. in a crucible gently till all the blue colour has disappeared, but not so high as to render the oxide of iron difficult of solution.

Dissolve in concentrated hydrochloric acid with the aid of heat. Filter off any insoluble. If any insoluble is present it is an indication that the blue has been adulterated. Test insoluble for barytes, silica, etc. Make up filtrate to 250 c.c. Pipette out 50 c.c. and estimate the iron by titrating with standard bichrome (see under Estimation of Iron in Iron Oxide, Chapter X.) by the usual method. The amount of iron (Fe) thus obtained multiplied by 3.03 gives approximately the amount of Prussian blue present.

Aluminium (Al_2O_3).—Pipette out another 50 c.c. and precipitate the iron and alumina with ammonia. Boil, filter, wash and ignite. Calculate the alumina by difference.

Calcium.—If present precipitate with ammonium oxalate.

Alkali Metals (Na and K).—To the filtrate from the iron and alumina add a few drops of hydrochloric acid, evaporate to dryness, and ignite to expel ammonia. Weigh; dissolve residue in a very small quantity of water, and the potassium is precipitated, and weighed as the double potassium platonic chloride. Calculate to KCl. Deduct weight of potassium chloride so obtained from the weight of the mixed chlorides, and the proportion of sodium chloride is found. Calculate to metallic sodium and potassium.

Cyanogen.—This may be estimated by the usual Kjeldahl method.

Analyses of samples of commercially pure Chinese blues give the following results :—

1	2	3
Alkali metal . . . 7.76	Moisture . . . 3.54	. . . 5.61
Iron . . . 39.69	Water comb . . . 18.18	. . . 15.46
Cyanogen . . . 52.25	Cyanogen . . . 41.10	. . . 37.72
	Iron . . . 32.16	. . . 29.48
	Alumina . . . 0.52	. . . 1.82
	Alkali metal (K) . . . 4.50	(Na) . . . 7.60
	Alkaline sulphate 2.31
	<hr/> 100.00	<hr/> 100.00

(1, Parry and Coste, "The Analyst," vol. xxi.

2 and 3, By the Author.)

Soda Blues, or Gas blues, are rather dirty Prussian blues, which have been made by substituting the prussiate of soda or soda ferrocyanide in place of the potash salt. Clean greens cannot be made from them.

Owing to the scarcity of potash salts during the war the use of soda blue came very much into vogue, but when the price of the potash salt approximates to that of the soda, it is very much more satisfactory and economical to use the former.

Specification for Prussian Blues.—The usual specification for a pure Prussian blue is as follows :—

1. The Prussian blue must consist of a ferrocyanide blue without the addition of any added matter whatever, such as alumina, zinc oxide, barytes, terra alba, and so on.

2. It should contain at least 20 per cent. of nitrogen and 30 per cent. of iron, and on ignition should leave about 30 per cent. of residue, all of which is wholly soluble in hot concentrated hydrochloric acid.

3. It should not contain more than 1 per cent. of matter insoluble in a 10 per cent. solution of oxalic acid.

4. It should not contain more than 1 per cent. of moisture, or 2 per cent. of matter soluble in cold water.

5. On reduction with zinc oxide in linseed oil in the proportion of 1 part of pigment to 50 parts of zinc oxide, the resultant shade should be equal to the standard blue similarly reduced.

Note.—If the Prussian blue is required for admixture with chromes for the production of Brunswick greens, then a Prussian blue with as little bronze as possible should be specified.

Brunswick Blue or Celestial Blue.—This blue is largely used in the paint trade *per se*, and for the production of Brunswick greens in association with the chromes.

It is manufactured by adding the requisite amount of the finest white barytes to the finished pulp Chinese blue in the vat, then pressing and drying. The amount of barytes added to the blue varies from 50 per cent. to 90 per cent., according to the quality required.

Brunswick blue has a beautiful pale blue shade, and is nice and soft in texture, and also easily powdered; on this account it has largely come into use. It is sometimes made in the dry way by adding the Chinese blue, a little at a time, to the barytes on the edge runners; but in this case the result is not so good, and the shade is not so well developed as by the wet method.

Terra alba is sometimes used in place of barytes, but this is unsatisfactory by reason of its woolly nature.

Three samples of commercial Brunswick blues analysed by the author gave the following results :—

	1	2	3
Moisture	0.75	1.20	0.50
Prussian blue . . .	12.50	23.80	10.75
Barytes	86.75	75.00	88.75
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

Soluble Prussian Blue.—Prussian blue, although insoluble in water, is soluble in oxalic acid, and this property is made use of for producing a "Soluble blue." This is made by dissolving the ordinary pulp Prussian Blue in a strong solution of oxalic acid and salting the dissolved blue out. The precipitate is filtered off, and the excess of the salts removed by washing with cold water.

Soluble blue can also be made by adding a solution of ferric chloride into an excess of potassium ferrocyanide solution. The composition of this pigment is represented by the formula $K_2Fe_2(CN)_{12}Fe_2$, a potassium-ferric-ferrocyanide.

It is less stable than the other forms of blue.

This blue was formerly used for making ink, but it has now been superseded by the aniline dyes. It is, of course, useless as a pigment in the paint trade on account of its solubility.

Turnbull's Blue (Gmelin's Blue).—This blue was formerly prepared by precipitating ferrous sulphate with potassium ferricyanide (K_3FeCy_6). It was supposed to have a different composition from that of Prussian blue, viz., Fe_5Cy_{12} , but has been proved to be identical with it.¹ It no longer comes on to the market under this name, having been superseded by Prussian blue.

Antwerp Blue.—This blue is still occasionally met with in the trade. It has a very pale blue colour, and may be described as a sort of Prussian blue lake, the base of which is alumina. It may be prepared by running a solution of prussiate of potash into a solution containing equal parts of ferrous sulphate, alum and zinc sulphate. It is chiefly used by artists.

A brief outline of the preparation and properties of the few remaining blue pigments that possess interest and are still used to a small extent for particular purposes will now be given.

COBALT BLUES

These blues are known in two forms, viz. (1) Smalts, a silicate of Cobalt, and (2) Cobalt Blue or Cobalt Ultramarine, which is an oxide of Cobalt.

(1) SMALTS

This pigment is essentially a cobalt glass. Its composition is roughly—

Silica (SiO_2)	60
Alumina (Al_2O_3)	15
Potash (K_2O)	17
Cobaltous oxide	0.8

It is prepared by fusing the cobalt ore with silica and potash. The cobalt glass thus produced is ground to a coarse powder. The strewing smalt obtained in this way was formerly much used by sign painters.

On further grinding under water to a very fine powder we get smalts produced which were formerly used by laundresses, in the pottery trades, and for giving a

¹ Prussian Blue and Turnbull's Blue v. Erich Müller [with Hans Lauterbach], "J. pr. Chem.," 1922 [ii], 104, 241–258.

blue tinge to writing paper ; also as a pigment in oil. The manufacture of artificial ultramarine has, however, caused this pigment to become obsolete.

(2) COBALT BLUE

(King's Blue, Cobalt Ultramarine, etc.)

This is an oxide of cobalt, and is one of the most permanent blue colours with which we are acquainted.

La Grange¹ states that the old masters used this oxide mixed with oil in their paintings, which is the reason why the sky and drapery in some old pictures are so durable a blue.

It is prepared by adding a solution of soda carbonate to a mixed solution of cobalt chloride, and alum, drying the precipitate, and igniting. It is then washed, dried and powdered.

Cobalt blue has a beautiful greenish-blue tint and is absolutely permanent. It is not acted on by heat, or readily by acids or alkalies. It is chiefly used as a pigment by artists, and in pale enamel tints and stoving enamels where absolute permanency is required ; also to a certain extent in the pottery trades.

It is a very costly pigment, and on this account is often adulterated with ultramarine blue.

Copper Blues.—The various copper blues, such as Bremen blue, mountain blue, blue verditer, are mainly basic copper carbonates (CuCO_3 , $\text{Cu}(\text{OH})_2$). At one time they were very largely used, but have now become practically obsolete because of their lack of body and liability to change under exposure to air and light. As their place has now been taken by ultramarine blue, it is necessary to enter into details regarding their manufacture.

¹ La Grange, "Manual of Chemistry," vol. i., p. 408.

CHAPTER IX

THE GREEN INORGANIC PIGMENTS

THE inorganic green pigments may, for convenience, be divided into two groups, viz. :—

(1) The naturally occurring green earth pigments and (2) the manufactured inorganic green pigments.

The important group of green pigments derived from the aniline dye-stuffs, such as naphthol greens, malachite greens, and others, will be discussed under the chapter on Lakes (see Chapter XIII.).

By far and away the most important of the manufactured green pigments in general use are the group known as the chrome greens or Brunswick greens, which are manufactured in enormous quantities for use in the paint, printing ink, and linoleum trades. They consist of mixtures of chromate of lead associated with Prussian blue and barytes in varying proportions.

The chief representative of the naturally occurring greens, and the only one which we will consider, is "Green Earth," a natural occurring "Augite," which is fairly widely distributed in various parts of the earth's surface.

(1) THE GREEN EARTH COLOURS

GREEN EARTH

(Terra Verte, Grüne Erde, Veronese Green.)

Green earth occurs fairly widely distributed in various localities. It is found in Germany, France, Italy, Cyprus, and in Cornwall.

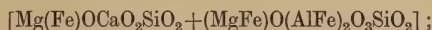
The shade ranges from a dirty green to a pale greenish grey tint. Being a natural earth it is, of course, quite permanent, and from very early times has been employed as a pigment, the brightest and cleanest shades being selected for this purpose. Owing, however, to its lack of body and covering power it has been replaced as a pigment by the many manufactured green colours that have been put on to the market in recent years.

Green earth is used in very large quantities in the colour industry on account of the peculiar property which it possesses of absorbing basic aniline dye-stuffs (see Lakes, Chapter XIII.), such as brilliant green, malachite green, auramine, methylene blue, and others, without the aid of any precipitating agent.

The German green earths are the best absorbents, and are readily capable of

fixing from 4 per cent. to 6 per cent. or more of these basic dye-stuffs. Moreover, they fix them so firmly that they are remarkably permanent and are unaffected by lime, so that by means of this earth we are enabled to produce a large range of lime fast colours, which are of immense value in the distemper industry.

Composition.—Green earth belongs to the very widely distributed group of earths or clays known as the augites, whose composition may be expressed thus :—



that is, a magnesium ferrous silicated aluminium oxide.

Analysis.—Analyses of German green earths by the author gave the following results :—

1		2	
Silica (SiO_2) .	40.6 per cent.	Silica (SiO_2) .	51.60 per cent.
Iron oxide (Fe_2O_3)	31.5 „	Iron oxide (Fe_2O_3) .	4.96 „
Alumina (Al_2O_3) .	6.5 „	Alumina (Al_2O_3) .	32.41 „
Calcium sulphate .	8.0 „	Manganese dioxide (MnO_2)	trace
Loss on ignition .	13.4 „	Magnesia (MgO) .	0.91 „
		Lime (CaO) .	7.06 „
		Sulphur trioxide (SO_3) .	2.74 „
	<u>100.0</u>		<u>99.68</u>
3			
Moisture .		0.5 per cent.	
Loss on ignition .		7.5 „	
Silica .		45.5 „	
Ferric oxide .		22.9 „	
Alumina .		8.5 „	
Lime .		1.5 „	
Magnesia .		5.2 „	
Potash .		7.5 „	
		<u>99.1</u>	

The green earths are prepared for use by a process of levigation, after which they are dried, ground and sieved.

To test the suitability of an earth for use as a base for the basic aniline colours, take 100 gms. and add a solution of 3 gms. of the dye-stuff in hot water, stirring well. All the dye-stuff should be completely absorbed. When tested under the palette knife it should be of a smooth texture and free from all coarse particles. It should also be of a clean tone, otherwise the resultant lake would be dirty and lacking in brilliancy.

(2) THE MANUFACTURED GREEN PIGMENTS

BRUNSWICK GREEN

(Chrome Greens, Vert de Chrome, Chrom Grüne, Milori Green, etc.)

Originally the name Brunswick green was given to the basic chloride of copper, a pigment which is now quite obsolete. At the present time—as we have already mentioned—Brunswick greens are by far away the most important class of greens at the disposal of the paint manufacturer, not only on account of their brilliancy, high covering power and comparative permanency, but because of the wide range of shades which they provide, according to the proportions in which the constituents of the pigment are associated.

Composition.—Brunswick greens are composed of a mixture of chrome yellow and Chinese blue, with varying amounts of barytes, according to the quality or grade of this pigment which the manufacturer desires to produce.

Pure Brunswick greens—that is, mixtures of chrome yellow and Chinese blue only—are rarely called for.

Manufacture of Brunswick Greens

There are two methods in general use for the production of these greens, which will now be described in some detail.

The Wet Method.—This method is the one generally adopted, because the green produced in this way is much brighter and more brilliant, and the admixture more perfect than by the “Dry Method.” Moreover, the tendency which these greens have to “float,” *i.e.* for the blue to come out on the top when made into paint, is thereby very considerably obviated.

The method of procedure is as follows:—

A chrome yellow is made according to one of the methods described under Lemon Chromes (see Chapter VII.), care being taken that the shade of the chrome is quite pale, or lemon yellow colour, and does not show any reddish or orange tinge in it.

The chrome is well washed to remove any soluble salts; then the required amount of fine barytes is weighed out and added to this pulp chrome. The amount of barytes added varies, of course, according to the quality or grade of the Brunswick green that is being made.

The barytes and chrome are then well stirred together till they are thoroughly mixed. Then a definite quantity of pulp Chinese blue is run in, with continuous stirring, until the desired shade is produced.

The manufacturer knows from previous trials the weight of dry chrome that his batch of pulp chrome contains, and also the percentage of dry blue in the pulp blue that he runs in, hence he can gauge the amount of blue required to a nicety. To check this a sample of the finished green can be taken out and dried in the laboratory, and compared against the standard.

The green is then given a wash with cold water, pressed and dried; then runnered in the edge runners, and sieved through 80-mesh sieves.

If the chrome has been made from lead acetate there is a tendency on drying out the green for it to turn dirty or "foxy," due to the formation of a basic or reddish chrome. This can be prevented by adding a little sugar of lead solution to the green just before pressing. In the case of lead nitrate chromes, which are more stable, this does not occur.

The Dry Method.—This method simply consists in mixing the required proportions of Chinese blue, lemon chrome and barytes, and grinding under the edge runners till the shade is fully developed. This takes from one to two hours, according to the size of the batch.

Another method consists in "runnering" or grinding the chrome with Brunswick blue to the required shade.

The Brunswick greens that are made are known in the trade under the following designations:—

(1) Pale Brunswick Green, (2) Middle Brunswick Green, (3) Deep Brunswick Green. Extra Pale and Extra Deep Brunswick Green are also made when specially required.

The difference between the various shades of Brunswick green consist merely in the amount of Chinese blue they contain.

Each of these shades of Brunswick green is made in five reduced qualities or grades, Nos. 1-5, No. 1 quality containing the least amount of barytes and No. 5 the largest.

Properties and Uses.—Brunswick greens are remarkable on account of their extraordinary good covering power and body. They possess beautifully bright and clean shades, and when made up into paint form work well under the brush.

They are fairly permanent on exposure to light and air, and, in addition to being noted for their excellent anti-corrosive and protective properties, are highly decorative and pleasing to the eye. Hence they are very largely used for both internal and external painting.

Very big quantities of Brunswick greens are also used in the linoleum trades at the present time.

Brunswick greens when made up into paint that is used in outdoor work tend after some time to become darker or bluer, and, in fact, after two years' exposure, in some cases it happens that the green colour has faded away and left nothing but the blue. This is due to the fact that the greens have not been properly prepared, traces of acid having been left in owing to faulty washing, and these acids have gradually dissolved out the chrome.

For use in distempers or as lime colours Brunswick greens are unsuitable on account of the fact that alkalies turn the chrome portion orange or red, and at the same time destroy the Chinese blue.

Exposure to acid fumes causes the greens to darken, and being composed of lead chromate they are naturally susceptible to sulphuretted hydrogen, which turns them black owing to the conversion of the lead chromate into lead sulphide. On

this account their use in gas-works or chemical works, where acid fumes are evolved, is precluded.

Specification for Brunswick Greens.—The usual specification is as follows :—

1. The Brunswick green shall be equal in colour and shade to the approved standard pattern.

2. It shall consist of a lemon yellow chromate of lead and Chinese blue (ferrocyanide blue) associated with barytes, and be free from any other added matter such as Paris white, terra alba, etc.

Note.—The amount of barytes may be stated here.

3. On reduction with ten times its weight of zinc oxide in linseed oil, the resultant shade shall be equal to the shade of the standard similarly reduced.

4. The Brunswick green shall not contain more than 1 per cent. of moisture, nor 2 per cent. of matter soluble in water.

5. The aqueous extract after shaking 10 gms. of the green with 50 c.c. of distilled water for one hour should be neutral to litmus.

Scheme for the Analysis of Brunswick Greens

(1) *Moisture.*—Weigh out 2 gms. and dry at 105° for two hours.

(2) *Insoluble.*

Boil 1 gm. of the Brunswick green with concentrated hydrochloric acid, taking down to dryness twice to make sure that all the lead sulphate is dissolved.

Filter off, wash well with boiling water, and dry on weighed filter paper = barytes + Prussian blue.

(3) *Prussian Blue.*—Gently ignite the insoluble residue to destroy the blue, and weigh. Estimate the iron present by potassium bichromate in the usual way, and calculate to Prussian blue by multiplying by 3.03. Barytes is got by difference.

(4) *Lead Chromate.*—Now proceed according to the scheme for the analysis of lead chromate (see Chapter VII.).

Analyses of Brunswick Greens.—The following analyses were made by the author on Brunswick greens which were being used in the manufacture of green paints in a large paint works, and will serve to give the reader a clear idea as to the composition of these pigments :—

Brunswick Greens

	No. 1 Deep.	No. 2 Middle.	No. 3 Pale.
Moisture	0.75	0.45	0.50
Barytes	60.28	72.35	85.75
Prussian blue	8.27	4.25	1.79
Chrome yellow	24.45	17.27	7.31
Lead sulphate	6.25	5.68	4.65
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00

Emerald Tint Greens.—These greens are similar in composition to the Brunswick greens, but are, as their name denotes, of a chalky, bluish, green shade, approximating to the colour of genuine emerald green.

Bronze Greens are dirty bronze shade greens, made from Brunswick greens, tinted with a considerable quantity of ochre and umber.

Coach Greens are a deep bluish clean shade green, and are made from nitrate chromes treated with a little nitric acid. They are usually toned up with a small quantity of Dutch pink.

There are many other Brunswick greens in common use of varying degrees of brightness and shade, such as the Royal greens, Albert greens, Moss greens, Hungarian greens, and so on; but as these can all be readily made from Brunswick green by the addition of tinters, a detailed description of them will not be necessary.

ZINC GREEN

(Vert de Zinc, Zinc Grün.)

Zinc greens have come rapidly into favour during the last twenty years, not only on account of their bright clean shades, but also on account of their permanency, which is far greater than that of the Brunswick greens.

These greens are composed of zinc chrome (zinc yellow), Chinese blue and barytes, and, unlike the Brunswick greens, are often sold in the pure state, *i.e.* without the addition of any barytes whatever. They are manufactured, as in the case of the Brunswick greens, either according to the wet method or by mixing dry under the edge runner.

Manufacture.—The best and cleanest shades are obtained, as with Brunswick greens, by adding the requisite amount of the pulp Chinese blue to the pulp zinc chrome, prepared according to the method described under Zinc Chrome (see Chapter VII.).

Large quantities are, however, made nowadays in the dry way by simply mixing the ingredients under the edge runner till the full shade of green is developed; this method gives excellent results, and at the same time, as will be readily understood, is much quicker and less costly than the alternative method.

Properties and Uses.—Zinc greens, equally with the Brunswick greens, can be made in a great variety of shades and qualities. The shades are clean and bright, of a fine smooth texture, and much more permanent than the greens made from the lead chromes; in addition these greens have the advantage of being non-poisonous. They are unaffected by sulphuretted hydrogen, and hence are largely used in oil as outdoor and indoor paints; they are also used for tinting enamels. Ground in oil they make very excellent protective and anti-corrosive paints, and retain their brilliant green colour in a remarkable manner.

Zinc greens would be much more widely used but for the fact that they do not possess so great body and obscuring power as the Brunswick greens, and also that in comparison they are much more costly.

This deficiency of obscuring power is due to the lack of body and strength of

zinc chrome component as compared with lead chrome. Zinc greens like Brunswick greens cannot be used as lime colours.

They do not show the objectionable tendency to "float"—that is, for the blue to come to the top—which is so noticeable with the Brunswick greens.

Analysis.—Two German zinc greens examined by the author had the following composition :—

1. Pure Deep Zinc Chrome.			2. No. 1 Pale Zinc Green.		
Zinc chrome	.	72.80	Zinc chrome	.	36.80
Chinese blue	.	23.70	Chinese blue	.	10.41
Zinc oxide	.	3.50	Zinc oxide	.	12.14
			Barytes	.	40.65
		<hr/> 100.00 <hr/>			<hr/> 100.00 <hr/>

Scheme of Analysis.—For a scheme of analysis for zinc greens the reader is referred to the chapters on zinc yellow and Prussian blue, since by simple modifications of the schemes there given no difficulty will be found in making an analysis of zinc greens.

Specification for Zinc Greens.—1. The zinc green must consist of zinc chrome and Chinese blue (and barytes for reduced qualities), and be absolutely free from all lead compounds such as lead chrome, white lead, etc.

2. It must be equal to the standard as regards shade and texture.

3. On reducing with 1 part of green to 10 parts of zinc oxide in linseed oil the resultant shade must approximate the shade of the standard similarly reduced.

CHROMIUM OXIDE GREEN

(Green Oxide of Chromium, Guignet's Green, Vert de Chrome, Grüne's Chromoxyd.)

Green oxide of chromium (Cr_2O_3) may be obtained by heating mercurous chromate in a retort till the whole of the mercury has distilled off. The residue chromium oxide possesses a beautiful bright greenish colour, and is one of the most permanent pigments that are known.

It is unaffected by heat or light, and can be boiled with acids and alkalis without undergoing change.

There are many ways of producing this pigment, of which we may mention the following :—

1. Calcining a mixture of 3 parts of neutral potassium chromate with 2 parts of ammonium chloride.

2. Calcining a mixture of potassium bichromate with either boric acid, sulphur or starch; by this means the chromic salt is converted into the chromium sesquioxide (Cr_2O_3).

The usual process in use on the large scale for the production of this colour consists in the calcination of potassium dichromate with boric acid, and it is desirable to describe this method in some detail.

Manufacture of Green Oxide of Chromium.—Guignet was the first to publish an account of the preparation of this green; hence the name “Guignet’s Green.” The green he prepared was the chromium tetrahydroxide of the formula $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.

In the form of a thick paste, and known as Guignet’s Green, this pigment is still largely used by calico printers. At the present time Guignet’s process is still, in all essentials, exactly as he described it; only in the furnaces where calcination takes place have there been any improvements.

The method of working is as follows :—

100 lbs. of potassium bichromate are ground up with 200 lbs. of boric acid so as to get an intimate mixture. The mixture is then put into a reverberatory furnace and heated for six hours to a dull red heat.

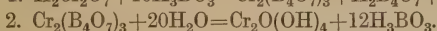
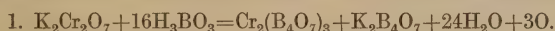
The whole mass fuses; a large amount of water is evolved, and a spongy mass of crude material is formed. After the reaction is complete the charge is raked out into vats containing cold water, and another charge is introduced into the furnace.

The fused mass is well lixiviated to remove all the soluble salts (potassium borate and excess boric acid), then ground under flat stones, dried and re-ground.

As a large excess of boric acid must be used to produce a bright shade of green, it is customary to collect the first wash liquors and precipitate out the boric acid by the addition of an acid.

The more dilute wash liquors are used to lixiviate the next batch of calcined crude material, and by this means raise the concentration of the solution so as to make the recovery of the boric acid worth while.

The course of the reaction may be expressed by the following equations :—



Properties and Uses.—The shade of chrome-green varies slightly according to the particular process of its manufacture, but as a rule it is a deep greenish blue colour.

Its covering power and strength are only moderately good. Its chief virtue lies in the fact that it is absolutely permanent, and for this reason is used in the engraving and the printing of bank notes. It can be mixed with any pigment without change, and has been used for producing a permanent green paint for stoving enamels. Acids, alkalies and heat have no action on it when properly prepared. Its more extended use is retarded on account of its comparative costliness.

Scheme for the Analysis of Chrome Greens.—The analysis of these greens is rarely called for, as a qualitative test will readily indicate if it has been adulterated with any other green pigment. If required, all that is necessary is to take 1 gm. of the pigment and fuse with ten times its weight of fusion mixture, and precipitate the chromium after reduction with ammonia. As this green is only used to a limited extent, there is no need to give a specification for it, as the properties required have already been fully mentioned.

The Copper Greens.—These greens were formerly very much used, but have

now been superseded by the more permanent Brunswick greens. The best known are (1) Emerald Green, (2) Verdigris, (3) Mineral Green, (4) Scheele's Green, and (5) Green Verditer.

We will now consider them briefly in the order of their importance :—

EMERALD GREEN

(Schweinfurth Green, Schweinfurtergrün, Paris Green, Imperial Green.)

Emerald green was first made in 1814 at Schweinfurt from arsenic and verdigris.

It is especially remarkable on account of the brilliancy of its colour, which is hardly equalled by any other known pigment.

Composition.—An aceto-arsenite of copper, it may be represented by the following formula : $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 : 3\text{Cu}(\text{AsO}_2)_2$.

In 1822 Liebig, the great German chemist, made a thorough examination of this green and published the following process for its preparation :—

Heat together equal parts of verdigris, acetic acid and white arsenic in twenty parts of water. Boil till the green develops, and add a little acetic acid from time to time to ensure that all the arsenite of copper is converted into the aceto-arsenite. Filter, wash and dry.

The process in use at the present time for the manufacture of this pigment will now be described in some detail :—

Manufacture. Raw Materials

The raw materials used for the production of this beautiful green are sulphate of copper, white arsenic, soda acetate, or acetic acid, and soda carbonate.

Care must be taken to see that the chemicals used are quite pure and free from iron ; if this is not done serious injury may result to the shade of the finished product. For this reason it is essential, before starting operations, to test out thoroughly all the chemicals employed as follows :—

Copper Sulphate.—The copper sulphate should first be tested by boiling up with dilute ammonia and filtering. Any reddish precipitate would indicate iron, and if present in more than minute traces the copper sulphate should be rejected as unsuitable.

White Arsenic.—1 gm. of the white arsenic should be sampled from bulk and ignited in a muffle in a fume chamber ; if it leaves more than 0.1 per cent. of residue it should be rejected as not being up to the required standard of purity.

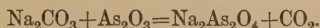
As a rule, in the case of acetic acid (or acetate of soda) and soda ash, the usual pure grades that are put on the market will be found satisfactory.

The process as carried out on the large scale is as follows :—The soda carbonate is dissolved in water in a copper steam-pan and half the required amount of the white arsenic carefully added. Steam is passed through till all the arsenic is dissolved ; then the rest of the arsenic is added and boiled till this is all taken up.

This process takes about six hours' hard boiling, and by this means (as is not

generally known) the soda carbonate is able to take up more than its theoretical amount of arsenic.

The white arsenic dissolves, forming arsenite of soda, and carbon dioxide is evolved thus :—



The resulting liquor of soda arsenite boils down to quite a syrupy consistency and must be diluted, and allowed to settle.

The sulphate of copper is next dissolved in the precipitating vat in a fairly concentrated solution (1 : 25) by the aid of heat and constant stirring. When it has all dissolved and the temperature of the solution is about 90° C., then the top liquor of arsenite of soda in the copper pan is next run in rapidly at the boiling temperature, with continuous stirring, care being taken to pass all this liquor through a fine sieve in order to remove any solid undissolved particles that may be present.

The requisite amount of a dilute solution of acetic acid (or its equivalent of a solution of acetate of soda) is next stirred in till the colour completely develops. Care must be used at this stage not to stir too much, as the beauty of the pigment depends on its somewhat crystalline nature, and the larger the particles the more brilliant is the resulting green.

The emerald green is next washed well to remove all soluble salts, then filtered and dried at a low temperature, and finally passed through coarse sieves, after which it is ready for use.

This pigment, on account of the arsenic which it contains, is exceedingly poisonous and dangerous to handle, and very special precautions must be taken during the whole process of operations to see that efficient ventilation is provided so that the workers do not inhale any of the dust.

From a theoretical consideration of the proportions of the various ingredients required for the production of this pigment, taken from the formula $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$; $3\text{Cu}(\text{AsO}_2)_2$, we obtain the following amounts :—

Soda ash	318 lbs.
White arsenic	594 „
Soda acetate	272 „
Sulphate of copper	1004 „

In practice, however, as already mentioned, it is found that only about half the above amount of soda ash is required.

An excellent emerald green can be made working with the following proportions :—

Soda ash	100 lbs.
White arsenic	200 „
Soda acetate	150 „
Sulphate of copper	250 „
Yield	<u>220 „</u>

Care must be taken to regulate the temperature of the reacting solutions to a nicety, otherwise the shade of emerald green will vary enormously. It has been found by long experience that the best shades of emerald green are produced round about 90° C.

Analyses of Emerald Greens.—The author has analysed many hundreds of samples of pure emerald greens at various times and they have all shown a remarkable uniformity of composition. The results obtained were as follows :—

	<i>Highest.</i>	<i>Lowest.</i>
CuO .	30·68 per cent.	30·20 per cent.
As ₂ O ₃ .	55·60 „	55·50 „

The complete analysis of an emerald green is rarely called for, but the following will serve to show the average composition of this pigment :—

Copper oxide	30·45 per cent.
Arsenious oxide	55·65 „
Acetic anhydride	13·90 „
						<hr/>
						100·00 „

Properties and Uses.—Emerald green possesses a beautiful bluish-green shade, quite characteristic of this pigment. It has fair body and covering power, and is moderately stable to light and air. It is wholly soluble in a solution of dilute ammonia, dissolving to a blue solution due to its copper content. It is also soluble in dilute acids.

Formerly emerald green was largely used in wall paper colours and in the manufacture of paints of that colour, as also for linoleums, toy paints, etc. Of late years, however, owing to its poisonous nature, it has been completely given up for this purpose. Large quantities, however, are still manufactured annually for use as an insecticide, both for home and export. Canada, and before the war Russia, used to take a large amount of this pigment to use as a fungicide, for which purpose, on account of its poisonous nature, it is extremely valuable. A certain amount is also employed in the manufacture of anti-fouling paints (see Chapter III.) for use in painting ships' bottoms to prevent the growth of weeds and barnacles.

Scheme for the Analysis of Emerald Greens

Copper.—Take 1 gm. of emerald green and dissolve in 20 c.c. hydrochloric acid; take down nearly to dryness, take up with about 30 c.c. water. Boil for several minutes. Wash into 8-oz. stoppered bottle. Bring slight precipitate down with caustic soda solution. Add a few drops of acetic acid in excess of dissolving precipitate, then add 40 c.c. of 10 per cent. potassium iodide solution. Add $\frac{N}{10}$ sodium thiosulphate solution from burette, drop by drop, taking care to add starch solution before end of reaction :—

$$1 \text{ c.c. } \frac{N}{10} \text{ Na}_2\text{S}_2\text{O}_3 \text{ solution} = \cdot 0063 \text{ Cu.}$$

Cu to CuO \times by 1.248.

Arsenious Oxide.—Take 0.5 gms. of sample, distil in flask with hydrochloric acid (H_2O to HCl), catch distillate in an alkaline solution (NH_4OH). Evaporate the contents of flask down three times with hydrochloric acid to make sure that all the arsenic comes over.

Acidify distillate with hydrochloric acid, leaving only a few drops of acid in excess. Add soda bicarbonate in excess. Titrate with $\frac{N}{10}$ iodine solution, using starch.

Double number of c.c.s. used and calculate, working on 1 gm.

$$1 \text{ c.c. of } \frac{N}{10} \text{ iodine solution} = \cdot 00495 \text{ As}_2\text{O}_3.$$

A quicker method for estimating the arsenic is as follows: Take 2 gms. of sample and dissolve up in 25 c.c. hydrochloric acid and 25 c.c. water. Keep solution at 180°F. for five minutes, cool, and make up to 250 c.c.s. in a measured flask.

Draw off 25 c.c. of solution ($= 2 \text{ gm. sample}$), place in No. 8 basin, dilute to about 300 c.c. bulk, and add solid soda bicarbonate, taking care to avoid spurting. Have large excess of soda bicarbonate.

Titrate with freshly standardised iodine solution, using starch.

Specification for Emerald Green

(1) The emerald green must be a pure aceto-arsenite of copper, and be equal in shade to the standard sample.

(2) On warming up with a dilute solution of ammonia, it must be completely soluble (0.5 per cent. of residue is permissible).

(3) On reducing with zinc oxide and linseed oil in the proportion of 1 part of emerald green to 10 parts of zinc oxide, the resulting shade shall be equal to that of the standard treated in a similar manner.

SCHEELÉ'S GREEN

This pigment was discovered by Scheele, the celebrated Swedish chemist, in 1778. It is an arsenite of copper with excess of copper hydrate, and has the formula CuAsO_3 ; $\text{Cu}(\text{OH})_2$.

It is prepared by dissolving arsenic in soda ash; then the hot solution of arsenite of soda is added to a hot solution of copper sulphate. The precipitate thus formed is washed with hot water and dried at a moderate temperature.

Scheele's green has a pale yellowish green colour, and possesses similar properties to emerald green. As a pigment it is in every way inferior to emerald green, and on the discovery of the latter in 1814 its manufacture fell away till at the present time it is seldom or never met with.

VERDIGRIS

(Basic Acetate of Copper, Vert de Gris, Grünspan.)

Verdigris has been used as a pigment from very early times. It has been detected in the wall paintings of Pompeii, in many of the early Italian pictures, and its virtues offered a subject of discussion to mediæval writers on the practice of painting.

Verdigris is a basic acetate of copper, and may be represented by the formula $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2, 2\text{Cu}(\text{OH})_2$. This pigment is now no longer used by artists, its place having been taken by the more permanent greens derived from chromium and cobalt.

Manufacture of Verdigris

(1) *French Process*.—The chief source of supply used to be France, where in former times it was a sort of domestic industry. Almost every vineyard produced a certain amount of this green as a side line and an additional source of revenue.

The methods in vogue are quite simple and crude, and consist in placing sheets or pieces of scrap copper in tubs along with the skins of grapes left after the juice has been pressed out. Acetic fermentation sets in, and after a few weeks' time part of the copper has been converted into the acetate of copper or verdigris.

When the grape skins are completely exhausted of acetic acid then the tubs are emptied out and the grape residue thrown away. The copper sheets, which are now covered with verdigris, are scraped clean, and are used over and over again with fresh supplies of grape skins till they are completely eaten away. The verdigris which has been scraped off the copper sheets is then collected in water, washed and dried.

(2) *Modern Chemical Process*.—The modern process for the production of this pigment is as follows :—

Take 160 lbs. of copper sulphate and dissolve in hot water, making the solution very concentrated ; then run in a strong hot solution of acetate of soda. Boil for two hours till the verdigris starts to separate out.

Cool ; throw on to strainers and wash sparingly with cold water. The reaction may be expressed by the formula $\text{CuSO}_4 + 2\text{CH}_3\text{COONa} = \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Na}_2\text{SO}_4$.

Properties and Uses.—Verdigris has a deep bluish green colour, and is of a coarse crystalline nature, hence it is rather hard in texture. It is slightly soluble in water, and very deficient as regards both body and covering power.

Like emerald green, it is completely soluble in ammonia. Its composition is roughly as follows :—

Copper oxide	43 per cent.
Acetic anhydride	29 „
Water	27 „

As a water colour it is of no use, as it rapidly fades ; in oil it is more permanent, but in time gradually goes black.

It is no longer used as a pigment, better greens having displaced it. Its chief

use at the present time is in anti-fouling compositions, its copper constituent rendering it destructive of all marine growths. A certain amount is used as verdigris paint in the tropics for the protection of wooden structures from the ravages of the white ant.

MINERAL GREEN

(Mountain Green, Malachite.)

This is a natural basic copper carbonate having the formula CuCO_3 , $\text{Cu}(\text{OH})_2$. The choicest specimens come from Siberia and Hungary. It is not now used as a pigment. The artificial mineral green that comes on to the market at the present time is of a different composition from the natural product, being as a rule simply a copper hydrate with a percentage of copper arsenite to brighten up the colour.

It is made as follows: 100 lbs. of copper sulphate are dissolved in hot water, and to this solution are added 50 lbs. of caustic soda solution, in which 20 lbs. of arsenic have been previously dissolved. Stir well, wash, filter and dry at a very low temperature.

This pigment is chiefly used as a poison in anti-fouling compositions, since as a pigment it is of little value, having all the usual defects of the copper greens.

Green verditer is a basic copper carbonate, but is of no value nowadays as a pigment.

CHAPTER X

THE RED INORGANIC PIGMENTS

THE red oxides or iron reds have been used as pigments from time immemorial, and even now form by far the most numerous and important group of colours used by the paint industry. This is due not only to their decorative effect, but also because of their great permanency, covering power and durability, combined with their cheapness.

These natural red oxides, or red earth colours, occur very widely distributed in different localities, and vary considerably both as regards purity and shade.

Large quantities, as we will describe later on, are also manufactured from artificial sources, such as waste residues containing iron.

Besides these red oxides of iron many other red colours are known which may be used as pigments, but those only will be described in detail which are at the present time of practical value and widely used as pigments, such as the red pigment obtained from lead and known as red lead, and the bright red from mercury known as vermillion.

For description of Chrome Red, see Chapter VII.

RED OXIDES OF IRON

These oxides are obtained, as already stated, from naturally occurring earths and also by artificial means.

(1) *Manufacture from Natural Earths*.—Oxides of iron are widely distributed in nature, and vary considerably as regards shade and purity, *i.e.* percentage of iron Fe_2O_3 . These deposits are found in various parts of England, America, Spain, France, Russia, India, and so on.

One of the finest and brightest shades of the naturally occurring red oxides that are known comes from Ormuz in the Persian Gulf, and is shipped in large quantities to this country to be worked up as a pigment. It is sold under the name of Persian Gulf Red Oxide.

Large deposits of very fine reds are mined in Spain and sold under the name of Spanish oxide; as a rule they contain over 80 per cent. of iron oxide (Fe_2O_3).

In France and England considerable quantities of red ochre from natural deposits are prepared for use as a cheap iron oxide pigment, and although low in iron content it has sufficient body and covering power to make it suitable for many purposes in

the paint trade. It comes on to the market under such designations as Venetian Red, Vandyke Red, Red Ochre, etc.

Native ferric oxide (Fe_2O_3) occurs largely in various parts of England in the minerals hæmatite, specular iron ore, spathic iron ore, limonite, and so on. But these, as a rule, lack the necessary shade and tone to be of any use as pigments until they have been worked up. Considerable deposits occur, however, of a purple colour, selected seams of which give us the well-known ranges of light, middle and deep purple oxides. These latter are very rich in iron, and contain generally over 90 per cent. of ferric oxide: they are largely employed for the manufacture of purple oxide and purple brown paints and colours. The process of converting the crude natural iron oxides into pigments is very simple, and usually all that is necessary is to grind it through special stone or steel mills to the required degree of fineness and then sieve.

In some cases, where much stone and earthy material is mixed with the crude earth, a grinding and levigating process is necessary in order to produce a material of a suitable degree of fineness.

(2) *Manufacture from Artificial Products.*—Large quantities of iron compounds which are by-products from various industries are worked up in different ways, so as to produce suitable coloured red oxides for use as pigments.

Among such by-products may be mentioned green copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) from galvanising works, waste iron residues from iron pyrites, which has been burnt to remove the sulphur content in the manufacture of sulphuric acid.

The red oxides of iron thus obtained vary very greatly in shade from light red to deep purple brown, according to the temperature at which they are “burnt” or heated. They are sold under such names as Turkey Reds, Venetian Reds, Bright Red Oxide, and Indian Red.

Process 1.—For the Manufacture of Turkey Red and Venetian Red

TURKEY RED OXIDE

(Colcothar, Caput Mortuum, Vitrioli, etc.)

Turkey red oxide varies in shade from a yellowish red to a bright deep red; it is one of the purest and strongest red oxides which are made. As a rule it contains from 93 to 95 per cent. of oxide of iron.

The process of manufacture consists in heating waste copperas (a by-product as already mentioned), which is usually obtained in the form of large slabs from galvanising works, in a large reverberatory furnace at a bright red heat.

The furnace is charged with the broken-up masses of copperas piled up about 12 to 24 inches high on the bed of the furnace. The fires are lighted and the whole mass heated strongly for eight to ten hours. The furnace doors are occasionally opened to rake over the mass of red-hot material so as to obtain even distribution of the heat, and also to break up the larger masses of material that cake together.

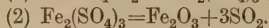
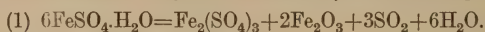
The furnace is connected by a long flue to a tall chimney in order to cause a strong draught to carry away the voluminous acid vapours produced.

When the iron oxide has reached the desired shade it is raked out hot and then well washed with water until all unburnt copperas is removed. It is then dried, crushed and sieved.

The lower the temperature the paler are the shades of Turkey red produced, some being a yellowish red shade containing only about 85 per cent. iron oxide.

Those produced at a higher temperature, and which are in most general demand, are of a rich bright red colour, and contain not less than 93 per cent. to 95 per cent. iron oxide.

The course of the reaction may be illustrated by the following equations :—



The escaping acid vapours are as a rule recovered and used to convert scrap iron into copperas for further burning.

In the manufacture of Nordhausen or fuming sulphuric acid the copperas is heated in earthenware retorts, and the products of distillation (*i.e.* fuming sulphuric acid) are collected in earthenware receivers.

The residue in the stills is known as *caput mortuum*, or *colcothar*, or jeweller's rouge. By whichever process these oxides are obtained they require to be worked up for use as a pigment by grinding in water, levigating, drying and sieving.

VENETIAN REDS

Originally Venetian red consisted of a natural occurring ferric oxide or red hæmatite, but now the bulk of the Venetian red that comes on to the market is obtained by calcining green copperas, or other similar waste iron residues.

The process of manufacture is similar to that described under Turkey reds. In this case, however, the copperas is mixed with whiting—more or less according to the quality of the Venetian red that is required. The mixture is then calcined on the bed of the furnace as mentioned above. The Venetian red thus produced does not require to be washed, but simply ground and sieved, and is then ready for use.



The Venetian reds are very bright shade oxides, and contain as a rule from 12 per cent. to 25 per cent. of iron oxides, though occasionally in their purest state they may reach 50 per cent. iron oxide.

Venetian reds are often made by simply grinding a very bright natural oxide or a Turkey red with *terra alba* to bring it down to the required shade and strength, and also at the same time to reduce its cost.

INDIAN REDS

These reds come on to the market in shades varying from light purple red to extra deep purple red. They contain generally over 90 per cent. iron oxide. Natural Indian red is a variety of pure red ochre or red hæmatite, and considerable quantities are imported from India.

These natural oxides are sometimes calcined to drive off the moisture, and so produce the required depth of shade. The bulk of the Indian red on the market is obtained by calcining copperas, or similar iron residues, in precisely the same way as described under Turkey Red.

The deep purple shades of the artificial Indian reds are produced by adding salt to the copperas during calcination and increasing the heat very considerably over a much longer period. They are then washed, dried and sieved.

RED OXIDE

(Red Ochre, Ruddle, Vandyke Red.)

The common red oxides of iron that are in use as pigments are mostly natural oxides associated with variable proportions of mineral impurities, such as silica, alumina, and calcium carbonate. The iron content is round about 50 per cent., but, of course, varies according to the source of supply. Some of these native red oxides or yellow ochres are calcined at a moderate heat, so as to drive off the water of hydration and thus produce the required shade. Others simply require putting through the usual levigating process.

MADDER INDIAN REDS, TUSCAN REDS

Red oxides are often brightened up with the addition of a permanent organic red such as alizarine lake, etc., and are then known as madder Indian, or Tuscan reds. These toners may be readily detected by boiling the red with an alcoholic solution of potash, when the dye-stuff is extracted.

Properties and Uses of the Red Oxides.—The red oxides of iron are one of the most permanent, and at the same time the cheapest, pigments available for the manufacture of all red paints and protective coatings. They have excellent body and covering power, and may be employed in conjunction with all other pigments without undergoing change. They are not affected by air or light, and after prolonged exposure show little or no sign of deterioration. Moreover, they possess very excellent protective and anti-corrosive properties, and are available in a large variety of shades, ranging from a pale yellowish red to the deepest purple.

They are not readily acted on by either acid or alkali, nor by sulphur gases, and withstand a considerable amount of heat without change.

For these reasons they are used in enormous quantities for painting all outdoor wooden or iron structures, for colouring cement, rubber, linoleum, lime colours, and other colouring purposes too numerous to mention.

Scheme for Analysis of Iron Oxides

The following scheme for the complete analysis of iron oxides may be used; as a rule, however, a determination of the iron content (Fe_2O_3) is all that is necessary.

1. *Moisture.*—Weigh out 2 gms. and heat in an air oven at 105°C . till constant in weight.

2. *Combined Water*.—Heat the above dried sample in a platinum crucible for two hours over a Bunsen burner to a dull red heat. Weigh till constant.

If carbonates or inorganic matter are present, then this must be taken into consideration and allowed for, otherwise the result should be expressed as “loss on ignition.”

3. *Insoluble Matter* (SiO_2 , BaSO_4).—Weigh out 1 gm. into a beaker, add 50 c.c. of concentrated hydrochloric acid, and take down to dryness twice to render the silica quite insoluble. Take up with a few drops of hydrochloric acid and 150 c.c. of hot distilled water.

Filter, wash well, and ignite; equals insoluble matter.

If barytes be present, and it is desired to separate the silica, then treat with hydrofluoric acid in a fume chamber. The insoluble residue should be quite white and show no reddish tinge, indicating that all the iron is dissolved out.

In the case of very difficult soluble oxides, such as the natural purple oxides, it is often found that the last traces of iron are hard to remove. In this case a good plan is to add a few drops of stannous chloride solution to the hydrochloric acid, which reduces the iron and facilitates its solution.

In the event of very refractory oxides it is sometimes necessary to fuse them with ten times their weight of fusion mixture (mixed carbonates of soda and potash) or else with potassium bisulphate before complete solution can be effected.

4. *Ferric Oxide* (Fe_2O_3).—The filtrate from (3) is made up to 250 c.c., and 50 c.c. are pipetted out into a white porcelain basin and brought up to the boil.

Stannous chloride solution is run drop by drop till all the colour is discharged—that is, all the ferric iron is converted into the ferrous state—great care being taken not to add any excess of stannous chloride solution.

100 c.c. of cold water are added, and when the whole solution is quite cold add 5 c.c. of mercuric chloride solution to remove any excess of stannous chloride. A very slight white milky precipitate is formed. If the solution turns black then the solution is too hot. If, on the other hand, a heavy milky precipitate is produced then too much stannous chloride has been used. In either of these cases it is better to throw the solution away and start afresh.

Now titrate with standard bichromate of potash solution, using potassium ferrieyanide as outside indicator. Check the result obtained by repeating the titration on another 50 c.c. of the solution.

5. *Alumina*.—Take 50 c.c. and add ammonium chloride solution and ammonia. Boil, filter and wash well with hot distilled water. Ignite and weigh as alumina and ferric oxide, the alumina being obtained by difference.

6. *Calcium*.—To the filtrate from the iron and alumina add ammonia and ammonium oxalate solution. Boil well. Filter, wash and ignite; equals calcium oxide.

7. *Magnesium*.—To filtrate from (6) add a solution of sodium hydrogen phosphate. Stir well and stand aside for six hours till all the magnesia has precipitated. Filter, wash and ignite.

8. *Carbonates* (CO_2).—Take 1 gm. and estimate CO_2 in the Schrötter apparatus. Calculate to CaCO_3 .

9. *Sulphate*.—Take 1 gm. and dissolve in hydrochloric acid. Remove iron and alumina as in (5), and precipitate the sulphates by the addition of barium chloride. Boil, filter and weigh as barium sulphate. Calculate to calcium sulphate.

The following analyses by the author on various oxides of iron will give a clear idea as to the composition of these pigments:—

	1	2	3	4	5	6	7
Moisture . . .	0.50	0.30	0.46	0.75	0.35	0.25	0.45
Loss on ignition . . .	1.42	2.25	1.35	3.25	7.94	1.15	2.38
Silica SiO_2 . . .	4.00	4.93	23.20	20.15	0.25	..	3.41
Iron oxide Fe_2O_3 . . .	90.05	85.25	64.00	55.50	82.54	95.32	90.00
Alumina Al_2O_3 . . .	2.85	4.53	7.65	15.45	3.25	3.28	2.41
Calcium CaO . . .	1.15	2.51	2.10	3.28	4.22	..	1.35
Magnesia MgO . . .	0.03	0.23	1.24	1.62	1.45
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>
		8	9	10	11		
Moisture . . .		0.20	0.35	0.45	0.63		
Loss on ignition	1.50	2.50	2.14		
Silica	2.00	3.25	1.85		
Iron oxide . . .		99.80	96.15	13.00	50.00		
Alumina	2.15	4.25		
Calcium sulphate	78.65	41.13		
		<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>		

1. Purple Oxide. 2. Spanish Oxide. 3. Persian Gulf Oxide. 4. English Red Oxide. 5. Turkey Red Oxide (yellowish red shade). 6. Turkey Red Oxide (bright red shade). 7. Black Oxide. 8. Super Deep Indian Red. 9. Super Light Indian red. 10. Common Venetian Red. 11. Best Venetian Red.

Specification for Red Oxide of Iron

The red oxide of iron must be a finely levigated pigment and contain not less than 80 per cent. of oxide of iron (Fe_2O_3).

It must be free from dye and any added materials such as barytes, Paris white, terra alba, silica, etc., and be equal in shade and texture to that of the standard sample.

On reducing the oxide with ten times its weight of zinc oxide in linseed oil, the shade thus produced must be approximately equal to that of the standard sample.

It must not contain more than 0.5 per cent. of moisture or more than 2 per cent. of matter soluble in water.

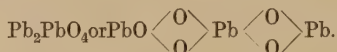
Note.—In the case of Venetian reds the amounts of ferric oxide content may

be specified as low as 12 per cent. Fe_2O_3 , whilst in the case of Turkey reds and Indian reds the percentage of Fe_2O_3 required will be not less than 90 per cent.

RED LEAD

(Minium, Mennige, Rosso Saturno.)

This valuable red pigment, under the name of minium, was well known to the ancient Egyptians. It is a lead tetroxide and may be represented by the formula Pb_3O_4 . In all probability it is a salt of plumbic acid, viz., lead orthoplumbate:—



Red lead is produced by heating litharge (PbO) in the air at a temperature of about 480°C . It is not, as was once supposed, a mixture of lead monoxide and lead peroxide ($2\text{PbO} + \text{PbO}_2$), for it has been shown that the dissociation pressure of lead peroxide at a given temperature is much less than that of red lead.

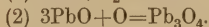
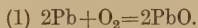
Commercial red leads always contain Pb_3O_4 with variable amounts of PbO ; this amount of free litharge averages between 6 and 12 per cent.

Manufacture of Red Lead.—In the manufacture of red lead the starting-point is metallic lead, and the process may be divided into two stages:—

(1) The conversion of metallic lead into massicot (lead monoxide). This is known as “drossing.”

(2) The transformation of this product into red lead (Pb_3O_4 ; $n\text{PbO}$).

The formation of red lead from metallic lead may be expressed by the following simple equations:—



The conversion of the metallic lead into the yellow lead monoxide or massicot is carried out on the manufacturing scale as follows:—

(1) *Formation of Massicot or “Dross”*

The pig lead is thrown on the bed of a reverberatory furnace and raised to a dull red heat. The molten lead thus obtained is stirred from time to time with long iron rakes so as to expose fresh surfaces of lead to the oxidising influence of the air, and as fast as the yellow scum forms on the surface of the lead it is raked to the back of the furnace.

Care must be taken not to raise the temperature too high, otherwise the scum or “dross” will be converted into the red litharge, which cannot be turned into red lead.

The operation of converting the metallic lead into “dross” takes from 12–24 hours, according to the size of the charge.

The yellowish coloured massicot is then raked out and ground under water

and levigated. By this means the unchanged lead is removed, and the fine yellowish lead monoxide is dried ready for the next operation.

(2) *Conversion of Massicot into Red Lead*

The yellow massicot is next introduced into the same furnace again and heated at a low red heat in the presence of a large amount of air to ensure perfect oxidation.

Care must be taken at this stage not to allow the temperature to get too high, otherwise the red lead would be decomposed according to the following reversible equation :—



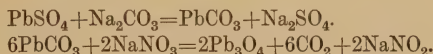
The operation takes about 12–15 hours ; towards the end of it samples are taken out from time to time and examined to see if the colour is up to standard. When this point is reached the contents of the furnace are immediately raked out.

The red lead is then finely ground and is ready for use as a pigment.

The manufacture of red lead, according to the above process, was originally only carried on in this country, and has attained a very considerable magnitude.

Of recent years, however, the Germans have adopted our processes, and now large quantities of this material are made in Germany. Big quantities are also made at the present time in the United States by the nitrate and the basic oxide processes (see below).

Red Lead from Lead Sulphate.—Another process for the manufacture of red lead—which, however, has not been carried on to any extent—consists in calcining a mixture of lead sulphate, soda carbonate, and soda nitrate together in a furnace. The reaction proceeds as follows :—



The fused mass is lixiviated with water, ground and dried.

Red Lead by the Nitrate Process.—In this process metallic lead and nitrate of soda are fused together, yielding an oxide of lead and nitrite of soda thus— $\text{Pb} + \text{NaNO}_3 = \text{PbO} + \text{NaNO}_2$. This oxide is washed to remove the nitrite of soda and calcined as above. The nitrite of soda thus recovered is used in the preparation of Para reds (see Lakes, Chapter XIII.).

The Basic Oxide Process.—In this process, recently worked out in the United States, molten lead is atomised, *i.e.* very finely divided by means of superheated steam. This is converted into a basic oxide by agitation with air and moisture, dried, ground, and calcined for twelve hours. This process gives an excellent fiery red lead.

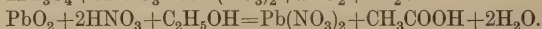
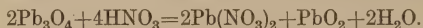
Properties and Uses of Red Lead.—Red lead possesses a bright scarlet red colour, and is very fine in texture. It has excellent body and is quite permanent, and has great density and hiding power. Its specific gravity is 8.6.

When heated gently in air the colour changes to a dark brownish red, but regains its colour on cooling.

When strongly heated it decomposes, giving off oxygen.

Red lead is completely dissolved by nitric acid in the presence of a reducing agent such as sugar or alcohol. This test furnishes a ready means of detecting the presence of any insoluble adulterants such as barytes, silica, and so on, which are left behind in the form of a white residue.

This reaction may be expressed by the following equations :—



When heated with hydrochloric acid, lead chloride is formed and chlorine given off; with sulphuric acid lead sulphate is produced with evolution of oxygen.

Red lead is largely used—made up into paint with linseed oil—as a priming or first coat for iron structures exposed to severe weather conditions. In fact, practically all first-class priming paints for iron and steel structures may be said to consist of red lead, or to contain a proportion of red lead as one of their constituents.

Besides possessing excellent anti-corrosive properties, red lead exerts also a very powerful drying action on oils, so that paints containing this material dry rapidly, and with a hard film or surface.

On account of this rapid drying or oxidising action of red lead on linseed oil it is customary to mix the red lead with the linseed oil just before using, otherwise the paint eventually sets up hard in the packages, rendering it unfit for use.

The hardening or “livering” of red lead ground in linseed oil is due to the litharge content.

Recently a non-setting brand of red lead has been put on the market to obviate this difficulty.

Red lead always appears to contain a certain amount of free litharge—sometimes as much as 25 per cent.—which may be removed by treatment with lead acetate solution.

On account of its hard-setting properties in linseed oil red lead is largely used in the making of hard-setting cements, lutes and packing for joints.

Red Lead Substitutes or Imitation Red Lead.—These are simply red dye-stuffs struck on barytes, with sometimes a proportion of red lead added.

Specification for Red Lead.—The red lead must be of a good bright colour, fine in texture, and equal in all respects to the standard.

It must be genuine and contain no added matter such as litharge, barytes, dye, whiting, etc. It must contain not less than 90 per cent. true red lead content.

It must contain not more than 0.5 per cent. of matter soluble in water.

ORANGE LEAD

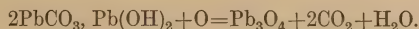
(Orange Mineral, Orange Mennige.)

This product has the same composition as red lead, but contains less free litharge.

It is prepared by calcining white lead, or more usually white lead residues or tailings, in a furnace similar to that used in the manufacture of red lead. The white

lead is heated at a low red heat for about twenty-four hours till the desired shade is produced.

The decomposition of the white lead proceeds according to the following equation :—



Properties and Uses of Orange Lead.—This pigment has a beautiful, bright, clean orange-red shade, and is exceedingly fine in texture. It is not so dense as red lead, having a specific gravity of 6.0.

The litharge content of orange lead is usually very low, and for this reason—unlike red lead—it may be ground into linseed oil or varnish without any fear of its “livering” or “feeding,” that is, setting up hard in the packages.

Orange lead is largely employed as a base for aniline colours—*e.g.* cosine on orange lead—on account of its excellent body.

It is very permanent and has excellent anti-corrosive and protective properties.

Scheme for the Analysis of Red Lead and Orange Lead

1. *Moisture.*—Take 2 gms. and heat at 105° C. Weigh till constant.

2. *Insoluble.*—Dissolve 1 gm. in semi-concentrated nitric acid, adding a little sugar, alcohol or other reducing agent. Dilute with boiling water. Filter if necessary, and wash well. Any insoluble denotes adulteration, and, if present, test for barytes.

3. *Total Lead.*—Evaporate filtrate to dryness; take up with as little hot water as possible.

Cool, precipitate with sufficient sulphuric acid; add a little alcohol, and allow to stand for one hour.

Filter through a weighed Gooch crucible, washing well with 50 per cent. alcohol. Dry and weigh as lead sulphate.

4. *Free Litharge.*—Weigh 5 gms. of the red lead and digest with a neutral solution of acetate of lead.

Filtrate through a Gooch crucible, wash well with boiling water, dry and weigh.

The weight of the residue subtracted from 5 gives the free litharge present.

5. *Dye-stuff.*—Boil up with alcoholic potash solution and filter. Any dye present will be at once apparent in the filtrate. This need not be estimated.

VERMILION

(Cinnabar, Zinnober, Vermilion.)

The mineral cinnabar or vermilion has been used as a pigment from the earliest days, and mention of it has been found as early as 600 B.C. It was used by the ancient Hebrews for painting the walls of their temples.

Pliny's “cinnabar” or “minium” was true vermilion, though it has often been confused with minium or red lead. It is a compound of mercury and sulphur (mercuric sulphide), HgS , and occurs naturally as the mineral cinnabar in Spain (Almaden), Austria (Idria), China, Japan, Mexico, Peru, and numerous other places.

The native cinnabar was converted into a pigment by carefully grinding selected pieces and sieving.

Although the ancients used the naturally occurring product, this has now been replaced by the manufactured article.

The Chinese have been renowned as makers of vermilion for many hundreds of years, and even at the present time the variety produced in that country is the most highly esteemed. The process of manufacture used by the Chinese has always been very jealously guarded, and kept in certain families, where it has been handed down from father to son.

MANUFACTURE

The methods in use for the manufacture of artificial vermilion may be divided into two classes, viz. :—

1. *The Dry Method*, in which the raw materials, mercury and sulphur, are combined in the dry state.

2. *The Wet Method*, in which the reaction is carried on in solution.

(1) *The Dry Process*

The dry method for the production of vermilion is the older method of the two, and is the one used by the Chinese, even at the present time. The Chinese method, with modifications, was introduced into Europe by the Dutch, who, however, were not particularly successful with their process. Later the manufacture was carried on in Austria by an improved method.

The original Dutch process was briefly as follows :—

20 lbs. of sulphur are melted up in an iron pan, and 100 lbs. of mercury gradually added with continual stirring. The action is a very vigorous one, great heat being evolved, and it must therefore be carefully regulated as so to avoid explosions.

When the reaction is complete, the fused black mass of black sulphides of mercury or “ethiops” is emptied out ready for the sublimation process. This latter is carried out in earthenware pots, or else in vertical iron cylinders fitted with heads and receivers. The pots or cylinders are placed in a furnace and so arranged that only the lower portion is heated. The “ethiops” or black mercury sulphide is charged into the pots or cylinders, which are then strongly heated, whereby most of the excess of sulphur is burnt off; and as the heat increases the vermilion sublimes on the upper and cooler portions of the vessels.

The pots are continually recharged, and when sufficient masses of sublimed red vermilion have accumulated, the pots are allowed to cool down and the vermilion is scraped off.

The vermilion is then ground and well washed with a fairly strong solution of alkali so as to remove the free sulphur and black sulphide of mercury that are present. Finally, it is well washed with cold water to remove all soluble matter, and dried at a low temperature.

Another method, which is an improvement on the Dutch process and gives a better yield, consists in mixing the sulphur and mercury in revolving drums for about

eight hours, whereby an intimate mixture of the materials takes place. The mixture of mercury and sulphur is then transferred to the sublimation pots, and treated as described under the "Dutch process."

(2) *The Wet Process*

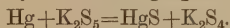
This process is the one that has been adopted by the English and German manufacturers of vermilion.

The original wet process was carried out as follows :—

300 parts of quicksilver are thoroughly ground with 68 lbs. of sulphur ; towards the end of the grinding operation a little caustic potash is added to complete the transformation of the mercury and sulphur into the black mercury sulphide. The black mercury sulphide is then warmed up with a strong solution of caustic potash and constantly stirred. After some time the black mass gradually turns brown, and then scarlet red.

Great care must be taken not to allow the temperature to exceed 50° C., otherwise the brilliancy of the colour will be impaired. Directly the red vermilion of the desired shade is produced cold water is run in and the vermilion well washed and dried.

An improvement on this process consists in shaking mercury with potassium pentasulphide at a temperature of about 45° for two or three days. The liquor is then run off and the residue treated with a concentrated solution of caustic potash till the bright red shade of the vermilion is fully developed. The reaction that takes place may be expressed by the following equation :—



This process gives an excellent yield, and the vermilion produced by it is equal in brilliancy to that of the vermilion obtained by the dry method. Moreover, it is very economical, as the mother liquor of potassium tetrasulphide only requires to be digested with flowers of sulphur to be reconverted into potassium pentasulphide, which may then be used over again.

Properties and Uses of Vermilion.—Vermilion is a bluish-scarlet red powder, and comes on to the market as pale vermilion or deep vermilion. The pale vermilion is obtained from the more crystalline deep vermilion by repeatedly grinding it till the required shade is produced. It has a specific gravity of 8.2.

It has very good body and covering power, and on account of its brilliant red colour was formerly very largely used, ground in oil and varnish, as a signal red paint. A little is still used by railway companies for this purpose, and also by coach-painters, who employ it as a lining colour. Owing to its costliness, however, and its tendency to turn black after long exposure, it has now been replaced by the cheaper permanent aniline (Alizarine, Fast Scarlet R) lakes. It is insoluble in alkalies and acids, such as hydrochloric or nitric acid.

On gently heating it turns brown, and then violet ; in the presence of air it burns with a bluish flame, leaving only about 0.1 per cent. of ash. This is the usual method of determining its purity.

Vermilion, as it comes on to the market, is rarely if ever adulterated.

Vermilion Substitutes or Vermilionettes are, however, sold in very large quantities. These are made by precipitating alizarine, eosine, Para reds, etc., on to barytes, or a mixture of barytes and orange lead (see Lakes, Chapter XIII.). They may readily be identified by—

(1) Ashing or igniting the sample and examining the residue.

(2) Warming with alcoholic potash solution and filtering, whereby the dye-stuff is extracted.

Vermilion is still a favourite pigment with artists.

It is used for colouring shellac and also in printing inks for special purposes.

Analysis of Vermilion.—A complete analysis of vermilion is very rarely called for, and in most cases it is quite sufficient to take 1 gm. and ignite in a crucible in a muffle furnace. Any ash more than 0.2 per cent. indicates adulteration.

If any ash be present, then boil with alcoholic potash and filter. If the filtrate is coloured, due to the presence of dye-stuffs, then proceed as described under the analysis of Lake Pigments (Chapter XIII.).

Specification for Vermilion.—The vermilion must be equal in shade and brightness to that of the standard, and be fine in texture.

It must consist of mercury and sulphur only, and on ignition leave less than 0.2 per cent. of ash.

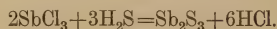
ANTIMONY VERMILION

(Antimony Orange, Antimonzinner.

Antimony orange is a compound of antimony and sulphur, and has the formula Sb_2S_3 . It is no longer used as a pigment in the paint industries, though a considerable amount is still used for colouring indiarubber in the rubber industries. It is made in two shades, orange and red.

The method used in the manufacture of this pigment consists in precipitating a solution of antimony chloride with a solution of hyposulphite of soda or lime at a temperature of about 70° C., and keeping at this temperature for two or three hours, with continual stirring, until the shade has fully developed.

It can also be prepared by passing sulphuretted hydrogen through a solution of antimony trichloride, or a solution of tartar emetic :—



CHAPTER XI

THE BROWN PIGMENTS

THE range of brown pigments is small, the chief ones of interest being the umbers and the Vandyke browns, both of which are natural earth colours.

RAW UMBER

(Raw English Umber, Raw Turkey Umber.)

This important earth colour is found in several parts of the country, also in France, Germany and America. The finest quality comes from Cyprus, and is known as raw Turkey umber to distinguish it from the poorer English umbers.

Composition.—Its composition is somewhat similar to that of the ochres and siennas, but differs from them in that it contains a considerably higher percentage of manganese in the form of MnO_2 or Mn_3O_4 . This earth is prepared for use as a pigment from the crude lump umber by the usual process of grinding and levigation.

Properties and Uses.—Raw umbers have a warm reddish brown colour with a greenish undertone; this undertone is especially noticeable in the raw Turkey umbers, and is due to the higher iron and manganese content as compared with English umbers, which are dirtier and duller in tone.

Raw umber is quite permanent, and mixes with all colours without change. It is very largely used as a stainer and tinter as well as a graining colour; it is also extensively employed in the manufacture of brown paints.

Raw umber paints work well under the brush, and owing to their manganese content dry off very hard and wear extraordinarily well.

BURNT UMBER

(Burnt Turkey Umber.)

Burnt umber is prepared by roasting the raw umber over a slow fire at a dull red heat till the desired shade is obtained. By this means all the water is expelled and the umber acquires a warm dark reddish-brown hue, which is very much appreciated.

This change of colour is practically due to the transformation of the brown ferric hydrate into the red ferric oxide.

Burnt umbers differ in quality and hue from the raw earth inasmuch as they are a darker and warmer brown shade, and also more transparent.

In addition to being used as stainers and tinters, and also in the manufacture of paints, a certain amount is used as a dryer in the varnish industry.

ANALYSES OF RAW AND BURNT UMBERS

The following analyses by the author will indicate the average composition of these pigments :—

	1	2	3
	<i>Raw Turkey</i>	<i>Burnt Turkey</i>	<i>Raw English</i>
	<i>Umber.</i>	<i>Umber.</i>	<i>Umber.</i>
Moisture	2.31	0.55	1.85
Loss on ignition	16.64	7.80	15.54
Silica (SiO_2)	16.60	22.75	31.56
Ferric oxide (Fe_2O_3)	39.95	49.81	25.76
Alumina (Al_2O_3)	4.60	1.89	9.45
Manganese dioxide (MnO_2)	11.50	12.00	6.42
Calcium oxide (CaO)	7.10	4.80	8.35
	<hr/>	<hr/>	<hr/>
	98.70	99.60	98.93

SCHEME FOR THE ANALYSIS OF UMBERS

Note.—This scheme is also applicable for all earth colours such as siennas, ochres, etc.

(1) *Moisture.*—Heat 2 gms. at 110°C . until constant. Loss in weight equals hygroscopic water (moisture).

(2) *Combined Water.*—Ignite the above dried sample in a platinum crucible over a low Bunsen burner. Loss in weight equals combined water.

Note.—Organic matter, and carbonates, would render the result inaccurate unless allowed for, hence this result is often expressed loss on ignition.

(3) *Insoluble Matter (Silica, Barytes, etc.).*—Digest 1 gm. of sample with 50 c.cs. concentrated hydrochloric acid and take down to dryness on the hot plate to render the silica insoluble. Filter, ignite and weigh. The residue, which should be white, consists of silica. Test with platinum wire to make sure no barytes is present. If barytes is present it may be estimated by removing the silica with hydrofluoric acid in the usual way.

(4) *Ferric Oxide (Fe_2O_3).*—Make up the filtrate to 250 c.c. and pipette out 50 c.c. into a basin and estimate the iron in the ordinary way by titration with standard bichromate of potash solution (see under Analyses of Iron Oxides, Chapter X.).

(5) *Alumina (Al_2O_3).*—Take 50 c.c. of the 250 c.c. in (4), dilute, add a little solid ammonium chloride and ammonia, and bring to the boil. Filter and wash. If manganese is present then dissolve the precipitate of iron and alumina thus obtained and re-precipitate, thus ensuring that any manganese that may have come down in the first precipitation is separated. Add washings and filtrate to the first filtrate. Dry, ignite and weigh; equals alumina and iron. Alumina is got by subtracting weight of iron obtained previously volumetrically.

(6) *Manganese.*—Take 0.5 gms. of the sample and add 30 c.c. concentrated

hydrochloric acid, and boil till the residue is white, indicating that all the manganese and iron has been dissolved. Then add a little sulphuric acid and evaporate down till all the hydrochloric acid is expelled, as evidenced by the evolution of sulphur trioxide fumes.

Cool, dissolve in a little water, and warm up till all the ferrous sulphate is dissolved. Bring to the boil and add zinc oxide paste (made by mixing pure zinc oxide in water) a little at a time. Keep adding the zinc oxide paste, while stirring, till all the iron is precipitated and some zinc oxide is left over.

Filter, wash well, and to the filtrate add about 3 grms. of acetate of soda. Bring to the boil and add a slight excess of bromine water. Boil well and then allow the precipitate of manganese to settle.

Filter, wash well with boiling water, and ignite; equals MnO_2 . If preferred the manganese may be estimated volumetrically by dissolving the manganese precipitate in dilute sulphuric acid and excess of oxalic acid and titrating back with standard permanganate solution. The volumetric method is very convenient where a large number of manganese determinations have to be made; it is also more accurate, as in the gravimetric estimation there is always some difficulty because the manganese precipitate adheres very firmly to the sides of the beaker and is very troublesome to remove.

(7) *Calcium* (CaO).—To the filtrate from the iron and alumina (5) add ammonium sulphide. Warm and filter off the manganese. Wash well and precipitate the calcium with ammonium oxalate. Filter and ignite; equals CaO .

(8) *Magnesium*.—Precipitate by adding soda phosphate in the usual way.

SPECIFICATION FOR BURNT TURKEY UMBER

1. The burnt Turkey umber shall be a genuine natural Cyprus umber, calcined to the same shade and depth of tone as the standard sample, and be free from all added matter such as barytes, silica, Paris white, etc.

2. It shall be finely levigated and free from all coarse particles.

3. It shall contain not less than 36 per cent. of iron estimated as Fe_2O_3 .

4. It shall not contain more than 1 per cent. of moisture and 2 per cent. of matter soluble in water.

5. On reduction with 10 parts of zinc oxide in linseed oil the resultant shade shall be equal to that of the standard similarly reduced.

The specification of a raw Turkey umber is as above, except it must be a genuine raw levigated Cyprus umber and contain not less than 30 per cent. Fe_2O_3 .

VANDYKE BROWN

(Cassel Brown, Cologne Earth.)

Vandyke brown derives its name from the great Flemish painter, who was particularly partial to the use of brown in his pictures.

At the present time far and away the best Vandyke brown comes from Germany.

It is manufactured from natural deposits of a brown earth, rich in organic matter, by very carefully heating so as to drive off all excess of moisture.

Sometimes various substitutes are sold as Vandyke brown which are very inferior as regards shade, and simply consist of mineral blacks mixed with ochre and umber to tone them up.

Properties and Uses.—Vandyke browns have a warm reddish-brown shade, rather transparent, and are of a woolly texture. It is sold ground in oil, in water, and in turpentine, and is largely used as a stainer and in graining work. It is a favourite water colour with artists, and is fairly permanent as such, but more so when ground up in oil.

Composition and Analysis.—As already mentioned, the composition of true Vandyke brown is mainly organic, and on ignition it only leaves about 10 per cent. of residue.

An analysis of two German Vandyke browns by the author gave the following results :—

1			2		
Loss on ignition .	.	90.34	Organic matter .	.	92.20
Ash ¹ .	.	9.66	Silica .	.	2.80
			Iron and alumina .	.	3.30
			Lime .	.	2.30
<hr/>			<hr/>		
100.00			100.60		
<hr/>			<hr/>		

Soluble Vandyke Brown.—When treated with alkalies Vandyke brown is rendered soluble, and in this form is largely sold as Vandyke crystals; the latter, which are soluble in water, are used in making walnut water stains.

SEPIA

This dark-brown colouring matter is obtained from the ink-bag—a weapon of defence—of the cuttle-fish (*Sepia officinalis*, *Loligo tunicata*), which abounds in the Mediterranean and Adriatic, and also off the coast of China.

This pigment is of a dark brown colour, and partakes of the character of a weak organic acid. It is prepared by dissolving the dried ink-bags from the cuttle-fish in a dilute alkali, straining and precipitating the colour with dilute hydrochloric acid, then washing and drying.

Sepia is used as a water colour by artists and is fairly permanent.

The other brown pigments, such as Prussian brown, bistre, Cappagh brown, are no longer of any general interest, and nothing is to be gained by describing them in any detail.

¹ The ash consisted of silica, iron and alumina, with a proportion of carbonates of soda and lime.

CHAPTER XII

THE BLACK PIGMENTS

THE black pigments that are in general use in the paint industry may be divided into two classes :—

1. The black earth pigments, which are prepared for use from naturally occurring substances such as coal, mineral black, graphite, etc., by a process of grinding and levigation.

2. The artificial black pigments such as lamp black, vegetable black, gas carbon black, ivory black, vine black, and others, which are obtained by imperfect combustion or charring of organic matter.

All organic black pigments contain carbon as their essential constituent, and while all these substances are said to be of a black colour, they naturally vary considerably both in shade and strength according to the amount of amorphous carbon they contain. Thus vegetable black, which is obtained by the imperfect combustion of oil, is practically pure amorphous carbon, and possesses far and away the best covering power and strength of all the black pigments in common use. Natural mineral black on the other hand often contains only about 30 per cent. of carbon, and is comparatively poor as regards tinting strength and covering power.

Carbon, as is well known, occurs in three allotropic modifications :—

- (1) The colourless, highly refractive crystalline diamond, which is one of the hardest substances known, and has a specific gravity of 3·5. Lavoisier, in 1772, was the first to show that the diamond was a combustible body, and that it yielded carbon dioxide; while Davey, in 1814, showed that carbon dioxide was the only product of its combustion, and hence proved that the diamond was pure carbon.

- (2) The soft, shiny, greyish-black amorphous graphite, also in the crystalline variety as a soft lamellar, scaly or flaky structure; its specific gravity is about 2·5.

- (3) The non-crystalline or amorphous form of carbon, which may be obtained by the decomposition of a great variety of carbon compounds, such as, for example—the most ancient of all—the conversion of wood into charcoal.

Carbon is an ideal pigment on account of its stability; it is unaffected by light and air. Acids and alkalies have also no action upon it; in fact, it is resistant to all agencies, and can only be destroyed by the aid of very high temperatures in the presence of air (combustion).

It may be noted here that paints made from carbon blacks, both natural and artificial, are rather slow drying; hence these paints require more than the average amount of driers.

The many methods in use for the production and preparation of these blacks, which are suitable for use as pigments in the colour industry, may now be described.

THE BLACK EARTH PIGMENTS

MINERAL BLACKS

True mineral black is a dry shale which occurs fairly widely distributed in nature. It is found in Spain, Germany, Italy, and many other places.

It is, as a rule, composed of about 30 per cent. carbonaceous matter and 70 per cent. of siliceous matter, though occasionally samples are met with having a much higher carbon content.

Many other forms of mineral black come on to the market, such as coal black (which is prepared from waste coal dust), slate black, and so on. Some of these are toned up by additions of crude charred matter, such as ground charcoal, lamp black, or other crude prepared blacks.

Mineral black is largely used on account of its cheapness in the manufacture of common black paints, sometimes a small amount of vegetable or carbon black being added to help to deepen the colour.

The following results obtained by igniting three different samples of commercial mineral blacks will indicate the variability of this pigment:—

	1	2	3
	Mineral Black.	Coal Black.	Slate Black.
Loss on ignition (carbon)	30.35	76.99	27.95
Ash	69.65	23.01	72.05
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00

BLACK OXIDE OF IRON

This black oxide pigment is a triferrous tetroxide, and has the formula Fe_3O_4 ; it occurs naturally as the mineral magnetite, and contains over 90 per cent. Fe_2O_3 (see Iron Oxides, Chapter X.).

GRAPHITE

(Plumbago, Black Lead, Reiss Blei.)

Graphite is widely distributed in different parts of the world. Large deposits are found in Ceylon, Madagascar, India, Siberia, United States, Canada, Bavaria, Bohemia, and other places. Big quantities of very fine black lead were formerly obtained from Borrowdale (Cumberland), but these deposits are practically worked out. Graphite also occurs in many specimens of meteoric iron.

The composition of a natural graphite from California is shown by the following analysis:—

Carbon	88.51
Ash	9.14
Volatile matter	2.35

Formerly graphite was supposed to contain lead; hence it was frequently called black lead and plumbago.

Artificial Graphite.—Molten iron dissolves considerable quantities of carbon, particularly if much silica be present. On cooling, part of this carbon is deposited in the form of black shiny crystals of graphite. Occasionally large quantities of graphite are found deposited in this way in iron-smelting furnaces; the name “kish” has been given to such deposits.

Graphite is also formed when charcoal or coke is heated to a very high temperature in the electric furnace out of contact with air.

Acheson's graphite is made at Niagara Falls by grinding coke with coal tar, molasses, etc., then heating in closed electric ovens to an extremely high temperature. It is then finely ground for use as a pigment.

Natural Graphite.—The great bulk of the graphite at the present time is obtained from the naturally occurring deposits in America, Ceylon, Bohemia, and other parts of the world.

The method simply consists in either a dry grinding of the selected material, or, in the case of the cruder sorts, levigating and grinding.

Properties and Uses.—The specific gravity of graphite varies from 2 to 3. It occurs in two forms—crystalline and amorphous.

Graphite is a soft, shiny, greyish-black substance, which is smooth and soapy to the touch. It is a good conductor of both heat and electricity.

On ignition in oxygen, graphite burns, forming carbon dioxide, and leaves an ash consisting of silica, alumina, and oxide of iron. When rubbed on paper, it leaves a black mark on account of its softness; hence the name “graphite” from the Greek “to write.”

Graphite is largely used in the manufacture of lead pencils. For this purpose the natural graphite is purified by grinding, and carefully washed free from gritty matter. It is then mixed with the finest washed clay, and the pasty mass forced by hydraulic pressure through perforated plates.

On account of its refractoriness graphite is also largely used in the manufacture of plumbago crucibles; in addition, it is employed as a lubricant, in battery plates, in anti-corrosive paints, in polishing gunpowder, in stove polish, and for many other purposes, too numerous to mention here.

As a pigment graphite has come very much to the front of late years, on account of its admirable anti-corrosive properties, and large quantities are used nowadays in the preparation of the many graphite anti-rust paints that are put on the market, and sold in very large quantities for painting iron structures, such as bridges, etc. (see Anti-Corrosive Paints, Chapter III.).

Graphite can be readily detected in a paint or pigment by simply rubbing a portion between the fingers, when it leaves a characteristic black shiny mark.

VEGETABLE BLACK

(Lamp Black, Soot, Lampenruss.)

The finest quality of vegetable black, which is nearly pure amorphous carbon, is obtained by burning mineral oils.

Process 1.—The process of manufacture is quite simple. Mixtures of mineral oil and mineral oil residues are fed from a tank or a constant level cistern into a series of lamps provided with burners and wicks, somewhat similar to the ordinary household lamp, by means of communicating pipes.

A large sheet iron funnel is placed over the flame so as to limit the air supply and just allow the oil to burn gently, and thus produce the maximum amount of soot.

From this funnel there is a slanting iron pipe through which the products of combustion and soot pass into a brick chamber. This chamber is connected with a series of cylindrical hemp or jute bags, through which the products of combustion and lighter soot pass and collect, the last bag being connected with the chimney. The bags can be opened at the bottom to remove the soot that collects from time to time.

The black that collects in the bags at the end of the series is the lightest and freest from oily residues and constitutes pure vegetable black of the finest and lightest quality.

The yield of black from this process is only about 20 per cent. of the oil consumed, hence it is a costly process.

Process 2.—The great bulk of the vegetable and lamp blacks which come on to the market at the present time is obtained by the incomplete combustion of such carbonaceous materials as rosin, tar, tar oils (creosote, etc.), naphthalene, mineral oil residues, pitch, and so on.

The process consists in charging a large movable, or fixed cast-iron pan with the oily or solid (usually a mixture of both) materials, and heating them up to the temperature of ignition, when they are set alight.

Several of these pans are connected with large iron pipes provided with a series of dampers for regulating the air supply leading into a long brick chamber about 90 ft. long by 10 ft. wide by 10 ft. high. The chamber is divided into compartments, an upper and a lower; each of these is subdivided into about six sections by means of brick walls three-quarter way up, so arranged that the products of combustion have to travel from section to section through the chamber till finally they come to a flue connected with the chimney.

The black gradually collects in the various chambers; the coarser blacks contaminated with oily particles being caught in the first chamber where they are collected and burnt over again. The finest and lightest blacks collect in the upper end chambers.

As a rule two qualities are collected: the finest and lightest in the end chambers—which is known as vegetable black; and the somewhat denser and heavier particles, known commercially as lampblack, in the other chambers.

The chambers are emptied from time to time by workmen who go in provided

with special clothing and respirators, and rake and brush out the accumulated black, which is packed straight into casks or bags.

During the process of combustion great care must be taken to regulate the heat and the air supply, for if there is too much air the combustion is carried too far, with considerable loss of black, and if, on the other hand, the temperature is allowed to get too high, then considerable amounts of oily material are volatilised or distilled over, spoiling the black formed in the earlier chambers.

Properties and Uses.—Vegetable black is one of the purest and lightest forms of amorphous carbon that is produced commercially. On ignition it leaves less than 0.1 per cent. of ash. Its specific gravity is 1.7.

Lamp black is not quite so pure, and leaves an ash often as high as 0.8 per cent.; and as we have already mentioned, it is considerably denser and heavier than vegetable black. The lamp black sold in packets on ashing is often found to give as much as 25 per cent. or more of residue. The latter cannot be described as pure lamp black, but a lamp black to which considerable quantities of other matter has been added as an adulterant.

Vegetable black is of a deep black shade, which on reduction with white lead gives a bluish-black tint.

Lamp black is not quite such an intense black, and is of a brownish-black colour.

Vegetable black is exceedingly fine and soft in texture, and has very great covering power and strength. It requires rather more than its own weight of oil to grind into a stiff paste. It floats on water without mixing, a circumstance due to its gaseous and oily content.

Largely used in paint, vegetable black is also employed as a tinter for various grey and slate-grey paints. It is also largely used in the manufacture of flat black paints and enamels, also for printing inks.

Specification for Vegetable Black.—1. The black shall consist of pure amorphous carbon only, and be equal in shade and density to the standard sample.

2. On ashing 1 gm. there must be less than 0.5 residue.

3. On extraction in a Soxhlet apparatus with ether, it must not yield more than 0.5 per cent. of oily residue.

4. On reducing one part of black with 100 parts of zinc oxide in linseed oil, the resultant shade shall be equal in tone and shade to that of the standard similarly treated.

5. It shall not contain more than 0.5 per cent. of moisture.

NOTE.—The specification for a lamp black should as a rule allow an ash content of more than 5 per cent.

CHINESE INK

(Indian Ink, Japanese Ink, Encre de Chine, Chinesische Tusche.)

This ink is essentially a very fine lamp black. The Chinese have prepared it from very ancient times by the imperfect combustion of oil in earthenware lamps. The soot formed is mixed up with fish-glue size, scented with musk or camphor, and moulded into sticks and dried. The ink is soluble in water and gives a bluish-black colour, which is quite permanent.

CARBON BLACK

(Gas Carbon Black, Gas Russ.)

This black comes exclusively from America, and is now used in large quantities in the paint and printing-ink trades.

As a rule it is sold in wooden cases of $187\frac{1}{2}$ lbs., and containing 15 paper bags, each weighing $12\frac{1}{2}$ lbs. It is sold under the different brands or marks of the various makers. The quality is, as a rule, about the same. There are, however, one or two particular brands which are about $2\frac{1}{2}$ times lighter or bulkier than the usual gas carbon blacks, and are sold for special purposes, such as the making of special printing inks.

Carbon black is obtained in America by burning the naturally occurring gases which come from the earth in such localities as Pennsylvania, Ohio and Virginia. It is calculated that it takes about 4000 cubic feet of natural gas to produce 1 lb. of carbon black.

The process of manufacture is very simple, and is as follows :—The natural gas is conducted through iron pipes to the brick chambers in which the gas is burnt. The flame from the ignited gas is made to impinge on to revolving drums, on which the carbon is deposited. As the drum revolves it automatically comes into contact with fixed sweepers which remove the carbon black deposited, which is subsequently collected.

The natural gas yields such a fine black that it needs no purification. As fast as it is produced it is carried away by moving hoppers and packed by machinery into bags ready for use.

Properties and Uses of Carbon Black.—Carbon black is of a very deep black colour, and is more granular and much harder in texture (and therefore requires much more grinding) than vegetable black. It is also considerably denser than the latter, and has a specific gravity of 1.85 to 2.10.

It is a pure amorphous carbon and leaves no ash on ignition. It is largely used in the paint and printing-ink trades.

Carbon black, when analysed, is found to consist of from 85 per cent. to 95 per cent. of amorphous carbon, from 1 per cent. to 7 per cent. of water, from 0.5 per cent. to 0.8 per cent. of hydrogen, and from 2 per cent. to 8 per cent. of oxygen (which is present partly in the H_2O of the water content).

Specification for Carbon Black.—It must be a pure gas carbon with not more than 0.5 per cent. ash, and equal in shade and strength to the standard sample.

IVORY BLACK

(Bone Black, Beinschwarz, Noir d'Ivoire.)

Ivory black was formerly made by charring waste cuttings of ivory in closed vessels, then grinding and washing and drying the resulting black residue.

At the present time ordinary bones are used, or more generally, glue works' residues, that is, bones which have been digested so as to remove the fat and glue from them.

The dried bones are crushed and packed into crucibles in order to exclude the air; they are then piled one on the top of the other in a sort of muffle furnace and heated for several hours till all the volatile matter has been driven off, leaving a black mass of bone charcoal behind.

In more modern works the process is carried out in large iron retorts so that the products of distillation—ammonia, Dippel's oil, or bone oil—can be collected and recovered.

The "char" or bone black that is left behind is ground, either coarsely if for sugar-refining purposes (*i.e.* as a decolorising agent), or else extremely finely for use as a pigment.

Properties and Uses of Ivory Black.—Ivory black is of a bluish-black colour and fairly smooth in texture. It is considerably denser than carbon black. Its specific gravity is about 2.68. Ivory black contains on an average 10 per cent. of carbon, 84 per cent. calcium phosphate and 6 per cent. calcium carbonate. It is used ground in oil as a paint and tint, and also in the printing and ink trades. Ground in turpentine and gold size it is employed by coach-builders as a body colour.

It is also sold under the names of animal black and jet black.

If the calcium phosphate and carbonate content be removed by digesting with hydrochloric acid, a fine black is obtained which commands a fancy price under the name of "black toner."

Like all the carbon colours, it is absolutely permanent and unalterable under all ordinary conditions.

It is often sold in the form of drops known as "drop ivory black."

VINE BLACK

(Rebenschwarz, Noir de Vigne, Frankfort Black, German Black.)

True vine blacks in their purest form are prepared by carbonising grape husks, vine twigs, washed wine lees, and so on. Other non-resinous woods and woody tissues are now also largely used, such as cocoanut shells, cork cuttings, twigs of beech and other woods, but the quality of the black is not equal to that of the true vine blacks.

The method of producing these blacks consists simply in packing the raw material in crucibles made of clay or iron, provided with luted covers to exclude excess of air, but at the same time allowing the products of the partial combustion or charring process to escape.

These crucibles are heated in a kind of muffle furnace, and when the issuing gases and moisture have ceased, the furnace is allowed to cool down and the contents of the crucibles are emptied out and recharged for the next operation.

This black is now often made by charring the woody materials in large retorts and collecting the products of distillation. This is especially the process in use for producing the cruder forms of vine black, which are really simply wood charcoals or charcoal blacks. The black residue is next very carefully washed, ground, dried and sieved so as to make it suitable for use as a pigment.

Properties and Uses.—Vine black is a beautiful bluish-black pigment, with great

depth of tone. On reduction with white it gives bluish-grey shades. It is largely used in the printing-ink trade and as a tinter for paints. Like all carbon blacks, it is quite permanent. Unfortunately at the present time large quantities of charcoal blacks are sold as vine blacks, and tinted up with Prussian blue so as to give the characteristic bluish-black colour.

Vine black makes a very good pigment for use as a water colour for artists.

It might be mentioned that this black is sometimes sold under the names of Frankfort black or drop black in the form of cones or drops. These drops are produced by mixing the black with a solution of glue and squeezing the pasty mass through tubes on to a board in the form of drops, then drying at a low temperature. More often however the drop black that comes on to the market is simply bone black made up into drops or cones, and may be readily identified by the large residue consisting of calcium phosphate which it leaves on ignition.

GENERAL SCHEME FOR THE ANALYSIS OF BLACK PIGMENTS

1. *Moisture*.—Weigh out 2 gms. on a watch-glass and heat at 105° C. till constant. Loss in weight equals moisture.

2. *Oily Matter*.—Extract 2 gms. in a Soxhlet's apparatus with ether and weigh the oily residue thus extracted.

3. *Ash*.—Weigh out 1 gm. into a crucible and ignite by strongly heating over a Bunsen burner until constant in weight. The residue may be quantitatively analysed if required, though as a rule a qualitative analysis is quite sufficient for most purposes.

4. *Carbon*.—This is obtained as a rule by difference, by adding together the oil, moisture and ash, and subtracting from 100.

The following analyses by the author will give an indication of the average composition of the various blacks that are in general use as pigments in the paint and printing-ink industries :—

	Drop Ivory Black.	Vegetable Black.	Carbon Black.
Moisture . . .	0.12	0.35	0.11
Oil	0.21	..
Ash ¹	81.00
Carbon	18.88	99.44	99.89
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00
	Common Lamp Black in Packets.	Vine Black.	Finest Lamp Black.
Moisture . . .	0.45	0.15	0.46
Oil	0.45	..	0.82
Ash ²	60.20	10.38	0.38
Carbon	38.90	89.47	98.34
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

¹ The ash is chiefly calcium phosphate.

² The ash is silica with traces of iron and alumina.

CHAPTER XIII

LAKES AND LAKE PIGMENT COLOURS

LAKES FROM NATURAL COLOURING MATTERS

LAKES are obtained by precipitating or fixing an organic dye-stuff on to an inorganic base, and are used in enormous quantities in the paint, printing ink and wall paper industries.

This class of pigments was used by the early Italian painters under the name of "lacca," which was obtained by precipitating certain natural dye-stuffs or lacs with tin and alumina compounds. Hence the derivation of the word.

The earliest lakes were, of course, all made from dyes extracted from the various natural occurring plants, woods, insects, etc., such as madder, logwood, Brazil wood, Persian berries, cochineal, indigo, and many others; but during the last half-century, owing to the enormous strides made in the development of the synthetic aniline dye-stuffs, especially in Germany, they have gradually fallen into disuse, and are now only employed for special purposes.

True lakes may be defined as transparent colours produced by precipitating the colouring matter (either natural or synthetic) on to a base of hydrate of alumina.

In recent years, however, this definition has become more generalised, and we have lakes on an alumina blanc-fixé basis. Further, to get more body for use in the enamel and paint industry, additions of such bases as barytes, zinc oxide, orange lead have been made to the true lakes, and thus we have what we may term the lake pigment colours, which possess very considerable body and covering power.

COCHINEAL LAKES

CARMINE LAKE, CRIMSON LAKE, MUNICH LAKE, VIENNA LAKE,
VENETIAN LAKE, SCARLET LAKE, PURPLE LAKE, ETC.

The raw material for the manufacture of cochineal or carmine lakes is the coccus cacti insect, which is indigenous to Mexico and Central America. These insects are collected from the trees on which they live by the natives, and are killed by dry heat in kilns. The dried insects come into commerce, packed in bags of about 160 lbs. each, under the name of Cochineal.

CRIMSON LAKE

The method used on the large scale for the production of this lake consists in digesting the powdered cochineal in a large copper—through which live steam is

passed—with a weak solution of carbonate of soda. After two hours' boiling the infusion is strained off into a wooden precipitating beek, and struck down by running in the requisite amount of 5 per cent. solutions of alum and cream of tartar.

Sufficient freshly precipitated and well-washed hydrate of alumina (White Base, see Chapter VI.) is then added in order to produce the required shade. The lake is washed three times, filtered and dried at a low temperature.

SCARLET LAKES

are prepared in a similar way to crimson lakes, but a certain proportion of genuine vermilion is added along with the hydrate of alumina so as to get the desired shade.

PURPLE LAKES

as crimson lake, with the addition of lime to produce the deep purple tone required.

CARMINE LAKES

The cochineal extract in this case is precipitated on to the alumina base as already described, but with the addition of chloride of tin.

Properties and Uses.—The cochineal lakes are used for colouring food and in cosmetics, but mainly in the preparation of fine coach body colours. They are gradually being superseded by the more permanent lakes made from the synthetic aniline dye-stuffs.

MADDER LAKES

These lakes were formerly made by extracting the dye from the madder roots and precipitating with a solution of alum. They have now been replaced by lakes made from synthetic alizarine (see Alizarine Lakes).

ROSE PINK

Brazil wood (lima wood or red wood) is digested in a boiler under pressure with a 5 per cent. solution of soda ash. The extracted liquor is run through sieves on to a base consisting of equal parts of Paris white and terra alba, then struck down with a weak solution of alum.

DUTCH PINK

Quercitron bark, indigenous to Brazil, is soaked for about ten days in a cold, weak solution of soda ash till the greater part of the colouring matter is extracted. The extracted liquor is decanted off and struck down on to a base of Paris white and terra alba with a weak solution of alum.

Properties and Uses.—Rose pink and Dutch pink are not much used nowadays owing to their fugitive and weak nature. They are used as toners (*e.g.* Dutch pink in Brunswick greens), also by scenic painters.

These natural dye-stuff lakes very often come on to the market in the form of

cones or drops. These drops or cones are produced by squeezing through funnels the pasty lake to which a little size solution has been added to act as binder.

BLACK LAKE

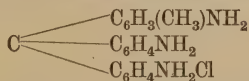
is made from logwood extract (hæmatein), by dissolving in a strong hot solution of soda ash, boiling with ferrous sulphate and bichromate of soda, then precipitating with sulphate of alumina.

LAKES FROM SYNTHETIC DYE-STUFFS

Historical.—At the present time the use of synthetic coal tar dye-stuffs in the manufacture of lake and lake pigments has developed to an enormous extent.

The founder of the synthetic coal tar dye-stuff industry, W. H. Perkin, laid down works for the manufacture of the first true aniline colour (mauve) at Greenford, near London, in 1856. He prepared mauve or mauvein (Perkin's violet), $C_{27}H_{25}N_4Cl$ or $(C_{27}H_{25}N_4)_2SO_4$, by the action of potassium dichromate on aniline obtained from coal tar. After this discovery a large number of chemists in England, France and Germany began to investigate the synthesis of colouring matters from coal tar.

In 1859 a French chemist, Verguin, discovered magenta (fuchsine), which was shown by A. W. Hofmann to be rosaniline hydrochloride :—



This discovery was closely followed by Hofmann's violet, Nicholson's blue, methyl violet and methyl green, and aniline black. In 1868 Perkin in England, and simultaneously Graebe and Liebermann in Germany, produced alizarine (the colouring principle of madder) from anthracene. The production of this synthetic dye-stuff was of immense importance, and its manufacture very soon displaced the natural product.

In 1874 A. Baeyer and Caro prepared fluorescein and eosin (tetra-brom fluorescein) by the interaction of phthalic anhydride with resorcinol, brominating the fluorescein to produce eosin.

If instead of phthalic anhydride, the di- and tetra-chlor substitution products are fused with resorcinol there is obtained in the phthalic acid residue, the di- and tetra-chlor fluoresceins, from which halogen substitution products, nitro-derivatives, ethers, etc., are produced, such as phloxine (dichlor-tetra-brom fluorescein) and rose Bengal.

Since 1887 the phthaleins have been on the market under the name of rhodamines, which are prepared in a similar way to that of fluorescein, except that instead of resorcinol, m-amido phenol, α -amido phenols substituted by alkyls in the amido-group are used. Rhodamine B being a diethyl (phenyl- etc.)-m-amido phenol phthalein.

Otto Fischer in 1877 discovered malachite green or bitter almond green by beating together dimethyl aniline and benzaldehyde with zinc chloride and oxidising the

leuco base thus formed. If, instead of dimethyl aniline, diethyl aniline is used brilliant green is produced.

Peter Griess, in 1866, discovered the diazo reaction and thus laid the foundation for the production of the insoluble azo and diazo colours which are one of the most important group of colours from which lakes and lake pigments are now obtained.

The list of colours of this group is immense and is increasing year by year as fresh applications of its derivatives are being investigated. To this class belong, for example, the Para reds, Lithols, Scarlets, Ponceaus, Bordeaux, to mention only a few examples in illustration of the immensity of the range of colours that are now being produced based on this reaction.

In 1880 Baeyer patented his process for the manufacture of artificial indigo, and by this process—modified and improved by other chemists such as Heumann, Sandmeyer, etc.—the Associated Aniline Companies of Germany (comprising the Badische Aniline Soda Fabrik, Meister Lucius & Brunning, etc.), manufacture yearly 95 per cent. of the total indigo consumed. There can be little doubt that it is but a question of time when the synthetic product will completely displace the natural indigo just in the same way that synthetic alizarine has displaced madder.

Although, as we have already shown, the synthetic dye industry was founded in this country by Perkin in 1856, it was left to Germany to develop its immense possibilities. That she has been able to do so to such a remarkable extent is due mainly to the large number of highly trained scientific investigators available in that country, and in a lesser degree to the fact that the industry has received State aid and has been unhampered by excise restrictions in the use of pure alcohol.

The formation of the British Dye-stuffs Corporation in 1919, and its manufacture of many of the dye-stuffs formerly imported from Germany, leads one to hope that this country will soon be self-supporting in the matter of the production of the synthetic dye-stuffs required by our industries.

Moreover, it is to be expected that with the large number of trained British chemists now engaged in the systematic investigation of synthetic dye-stuffs our dye factories will, in the course of time, bring out new and more permanent series of dye-stuffs, which will gradually replace those now in use. For the manufacture of lake and lake pigments the question of a large range of permanent dye-stuffs suitable for the production of lakes of a bright and permanent character is of the utmost importance. But at the same time their cost must not be prohibitive.

The manufacture and properties of the most important synthetic dye-stuff lakes used in the paint trade must now be considered.

MANUFACTURE OF LAKE PIGMENTS FROM THE SYNTHETIC DYE-STUFFS

It is usual to group the synthetic dye-stuffs employed in the manufacture of lakes and lake pigments according to their methods of precipitation as follows :—

- (A) Acid dye-stuffs precipitated with barium chloride.
- (B) Basic dye-stuffs precipitated with green earth (or white earth).

- (C) Resorcin dye-stuffs precipitated with lead acetate or nitrate.
- (D) Diazo dye-stuffs precipitated by diazotising or coupling.
- (E) Mordant dye-stuffs precipitated on alumina such as Alizarine (formerly called adjective dye-stuffs).
- (F) Insoluble pigment dye-stuffs.

The above classification is, of course, only a general one, and there are many exceptions as one would naturally expect.

The Base.—The base or carrier for the dye-stuff must be very carefully chosen if the best results are to be obtained. For example, a dye-stuff struck on a base might be quite suitable for the manufacture of a paint, but unsuitable for use as a distemper or printing-ink colour. Hence the purpose for which the lake is going to be used must be carefully thought out by the lake manufacturer.

Alumina.—The most suitable base for the manufacture of fine lakes for the printing-ink and wall-paper trades is alumina. The lakes formed on this base are of great transparency and brilliancy of colour. Blanc-fixe alone or in combination with alumina makes a splendid base of good covering power and of excellent fineness and texture. This base is very suitable for fine enamel colours.

Barytes, being very cheap, is the base most commonly used. Care must be taken that it is fine and absolutely free from all grit. It must be of a good white colour, free from iron, and contain no acid or alkali.

Terra alba, whitening, catalpo and china clay are also employed as bases according to their suitability for the special purpose for which the lake is intended to be used.

Zinc oxide, white lead, red lead and orange lead are used in conjunction with the above bases in special cases to act as toners where a particular tone or shade is required.

A. ACID DYE-STUFFS PRECIPITATED WITH BARIUM CHLORIDE

The manufacture of these lakes is carried out as follows :—The dye-stuff is dissolved in boiling water, about 1 part dye-stuff to 100 parts water, then run into a large wooden vat provided with mechanical stirrers (see Fig 16). The base is next added and the stirrers set going, and when the right temperature has been reached (about 80° C.), the requisite amount of the barium chloride (iron free) solution is run in till complete precipitation has taken place.

To make sure that all the dye-stuff is precipitated, a portion is taken out and filtered to see that the liquor is free from any dye-stuff in solution. A quicker method is to take out a portion and spot it on filter paper and hold it up to the light. If complete precipitation has taken place, the wet spot round the lake will be colourless. The lake is well washed, filtered and dried at a low temperature.

Examples.—The following examples will best illustrate how these lakes are produced. It must, of course, be understood that the examples given are only to be taken as a general indication of how the lakes are manufactured. The best results can only be obtained by studying each individual dye-stuff and finding out by experiment which is the most suitable for the particular purpose required.

Scarlet Lake

(1) Brilliant Lake Scarlet G . . .	32 lbs. (1 : 100)
Best barytes	156 „
Barium chloride	32 „ (1 : 10)
	<hr/>
Yield	190 „

Brilliant Turkey Red Lake

(2) Brilliant Lake Scarlet G . . .	20 lbs.
Ponceau 2 R	4 „
Barytes	500 „
Barium chloride	20 „
	<hr/>
Yield	528 „

(3) Blanc-fixe or best barytes . .	112 lbs. in 15 gals. water
Brilliant Scarlet 2 R . . .	5½ „ (1 : 30)
Barium chloride	5½ „ (1 : 10)
	<hr/>
Yield	115 „

Temperature of precipitation, 90°–95° F.

(4) Precipitating Acid Dye-stuffs on Alumina—Blanc-fixe

17–18 per cent. Sulphate of alumina	112 lbs.
Soda ash	50 „
Naphthol green B	34 „
Barium chloride	136 „

Dissolve the sulphate of alumina in 120 gallons of cold water. Precipitate by adding the soda ash dissolved in 50 gallons of hot water. Stir and add the naphthol green B dissolved in 100 gallons of hot water; then add the barium chloride dissolved in 80 gallons of hot water. Wash, filter press and dry in the vacuum stoves.

Note.—This naphthol green lake is very fast to light and lime, and hence is very largely used as a distemper colour.

Alternative methods to this last formula are (1) to split the soda up into two parts, or (2) to split up the sulphate of alumina.

1. 17–18 per cent. Sulphate of alumina . . .	112
Soda ash	20
Naphthol green B	34
Barium chloride	136
Soda ash	30

2. 17-18 per cent. Sulphate of alumina . . .	56
Soda ash . . .	50
Naphthol green B . . .	34
Barium chloride . . .	136
Sulphate of alumina . . .	56

The two-soda or two-alum process is very useful in those cases where difficulty occurs in striking down the dye-stuff completely by the direct process. Moreover, in some dye-stuffs the resultant lakes are more brilliant and permanent than those obtained directly.

B. BASIC DYE-STUFFS PRECIPITATED BY GREEN EARTH, TANNIN, TANNIN AND TARTAR EMETIC, KATANOL, ETC.

The well-known capacity of green earth (or white earth) (see Chapter IX. to absorb many basic dye-stuffs is largely taken advantage of in the production of lime fast colours, for use in distempers and kalsomines. The method is extremely simple and is as follows :—

Example 1.—Green Earth Carrier.

Green earth . . .	112 lbs.
Malachite green . . .	2 „
or Brilliant green crystals . . .	2 „

Example 2.—White Earth Carrier.

White earth . . .	112 lbs.
Methyl violet B . . .	2 „
or Methylene blue B . . .	2 „
extra concentrated.	

The green earth or white earth is mixed into a thin sludge with cold water. The dye-stuffs dissolved in 25-50 times their weight of hot water are run in, with continuous stirring, till all the dye-stuff is taken up. Filter press and dry.

A good German green earth is capable of absorbing from 4 per cent. to 6 per cent. of its weight of basic dye-stuff, this being due to the formation of insoluble silicates with the dye-stuff.

Example 3.—Precipitating by Tannin on China Clay

China clay . . .	100 lbs.
Auramine O . . .	2 „
Tannin . . .	5 „
Soda acetate . . .	1½ „

Method.—Mix the china clay to a paste with 15 gallons of water. Add while stirring the 2 lbs. of auramine O dissolved in 10 gallons of water. Then precipitate by the addition of 5 lbs. of tannin and 1½ lbs. of soda acetate 1:10. Filter and dry.

This precipitation is due to the formation of insoluble tannates with the basic dye-stuffs. Temperature of precipitation about 150° F.

Example 4.—Precipitation with Tannin and Tartar Emetic on Hydrate of Alumina

Hydrate of alumina	100 lbs.
Methylene blue	50 „
Tannin (neutral)	50 „
Tartar emetic	50 „

Method as Example 3. The tannin tartar emetic lakes are much faster and brighter than the tannin lakes.

Tamol N (B.A.S.F.) and Katanol (Bayer)

The new precipitants tamol N (B.A.S.F.) and katanol (Bayer) have recently been introduced for producing lakes from the basic dye-stuffs in place of tannin, and present many advantages over this substance. The lakes thus produced are not so spongy as the tannin lakes and are superior as regards covering power and fastness to light.

Bayer's katanol, a moss greenish powder smelling somewhat of iodoform, is a thiophenol, whilst the Badische tamol, which is a combination of formaldehyde and naphthalene sulphonic acid, is a liquid. Both require to be neutralised with soda ash before use.

The following brief description of the manufacture of two katanol lakes will illustrate the method used in the production of these lakes (Bayer, 1921).

Barytes Lake

Barytes	100 lbs.
Rhodulin blue 6 G	2 „
Katanol	1 „ +0.25 soda ash
17-18 per cent sulphate of alumina	$\frac{1}{2}$ „	1 : 10

The katanol solution is made as follows :—

Katanol	100 gms.
Soda ash	25 „
Boiling water	1 litre

The dye-stuff is dissolved in fifty times its weight of hot water, run on to the barytes, stirring continuously.

The katanol solution is then added till precipitation is complete. The excess of soda is neutralised by the addition of the requisite amount of a 10 per cent. solution of sulphate of alumina.

Alumina Blanc-fixe Katanol Lake

17-18 per cent. Sulphate of alumina	10 lbs.	1 : 10
Soda ash	4 „	1 : 10
Barium chloride	11 „	1 : 10

Wash the precipitate thoroughly, then add :—

Victoria blue B	3 „	1 : 50
Katanol solution	$13\frac{1}{2}$ „	

This makes a very fine bright fast lake suitable for lithographic prints and paper staining.

Other methods of precipitating these basic dye-stuffs which may be mentioned are by resin soap, Turkey red oil, casein, phosphate and silicate of soda, but we have not space to go further into these processes, which are only of minor importance.

C. RESORCIN DYE-STUFFS PRECIPITATED WITH LEAD NITRATE AND LEAD ACETATE

This group of colours consists chiefly of Eosine, Erythrosine, Phloxine and Rose Bengal.

From these dye-stuffs are obtained the well-known vermilionettes and geranium lakes which are in large demand on account of the brilliance and beauty of their shades. Unfortunately they are not permanent, and hence are not suitable for use in paints or enamels which are made for outdoor work, being replaced for this purpose by the more permanent Para and Lithol reds.

Their method of preparation is exceedingly simple, as the following examples will show:—

Example 1

Barytes	100 lbs.
Eosine A 5 G	2½ „
Lead nitrate	2½ „
Water	2 gals.

Dissolve the eosine in thirty times its weight of boiling water and run on to the barytes mixed to a thin paste with hot water, stirring continuously. Strike down the colour with a hot solution of nitrate of lead.

Example 2

Barytes	100
Red lead	100
Eosine 2 G	2
Phloxine	1
Lead acetate	3

Example 3

Blanc-fixe	100
Orange lead	100
Eosine 1136	3
Rose Bengal	1
Lead acetate	4

Precipitate as before. Temperature of precipitation 90° F.

D. THE INSOLUBLE AZO AND DIAZO DYE-STUFFS

The discovery of the diazo reaction by Peter Griess in 1866 opened up the way for the production of an immense range of the most important dye-stuffs for the manufacture of lakes of great brilliancy and permanency, such as the Para red, Lithols, Fast Scarlet R, etc.

The formation of the dye-stuff consists, in its simplest form, in the diazotising the aromatic amines, and then coupling the diazo compound thus formed with a naphthol.

We will now give a few examples illustrating how this class of lakes is produced :—

Para Red or Para Nitraniline Lake

This is one of the simplest and earliest of the diazo colours, and its preparation will now be described in detail so as to give a clear insight into the basis on which this most important and valuable range of permanent reds is produced.

(1) *The Diazo Solution* is made up as follows :—

44 lbs. 15 ozs. Para nitraniline are made into a paste with $8\frac{3}{4}$ gals. of cold water to which 119 lbs. hydrochloric acid 32° Tw are added.

After a further addition of 33 gals. of water—as cold as possible— $24\frac{1}{4}$ lbs. nitrite of soda just previously dissolved in 11 gals. cold water are poured in (in one portion) and then 88 lbs. 3 ozs. acetate of soda 1 : 3 is added.

Then strain and fill up with cold water.

(2) *Naphthol Solution*.—To 50 lbs. beta naphthol or beta naphthol R pour 110 gals. of hot water and 4 gals. soda lye 76° Tw. Then add 36 lbs. $5\frac{1}{2}$ ozs. soda ash and 22 lbs. Turkey red oil.

Stir well until solution has taken place, fill up to 220 gals. and allow to cool.

(3) *Precipitation of the Lake*.—1102 lbs. barytes are stirred into the cooled-down naphthol solution. To this the diazo solution is slowly added whilst continuously stirring. Allow to stand $\frac{1}{4}$ hour, stirring occasionally. Pour the lake on to a filter, wash well with cold water, press and dry at about 120° F.

Beta naphthol R gives lakes of a bluer tone than beta naphthol. Usually the diazo solution is cooled down with ice, hence the name ice colours given to these lakes.

Properties and Uses.—Para reds are very largely used in the manufacture of signal red paints and enamels, and post-office reds. They are brilliant in hue and fairly permanent, but have a tendency to bleed. They are moderately fast to lime and spirit. At the present time they are gradually being replaced by the newer and more permanent reds, such as Helio Fast red, Lithol red, etc.

This dye-stuff is on the market as Para toner, Autol red B L (Badische), Pigment red B (Meister Lucius & Bruning), and so on.

Bordeaux Lake

(Alpha Naphthylamine Lake.)

This deep red or claret shade lake is made in the same way and by the same reaction as the Para red, but in this case the Para nitraniline is replaced by alpha-naphthylamine.

Properties.—A deep bluish claret-coloured lake, with a deep blue undertone, fairly permanent to light and lime.

We will now consider the preparation and properties of one of the most valuable and permanent reds on the market as far as the lake manufacture is concerned, viz. :—

Helio Fast Red B L (Bayer)

[Sitara Fast Red, Lithol Fast Scarlet R (Badische), Permanent Red 4 R (Berlin Aniline Co.), Monolite Fast Scarlet R (B.D.C.)]

According to the method of Weiler-ter-Meer the process for the production of this extremely fast red is as follows :—

(1) *Naphthol Solution*.—16 lbs. $1\frac{1}{2}$ ozs. beta naphthol, together with 12 lbs. 9 ozs. soda lye are dissolved in 22 gals. of hot water. This solution is then made up to 220 gals. by means of cold water. Add 24 lbs. 4 ozs. soda ash, dissolved in 22 gals. of water.

The temperature of these solutions should be about 60°–70° F.

(2) *Diazo Solution*.—102 lbs. 9 ozs. pure hydrochloric acid 32° Tw are poured into 11 gals. boiling water. To this add carefully $16\frac{3}{4}$ lbs. meta nitro Para toluidine, whilst stirring briskly at a temperature not below 210° F., so that solution takes place at once.

The meta nitro Para toluidine should be run in within 3 to 5 minutes. The total volume of the perfectly clear solution should amount to 23–24 gals. This solution is then (whilst well stirring) poured slowly into 44 gals. of water and 178 lbs. 10 ozs. ice. Finally, whilst briskly stirring add all at once 7 lbs. 15 ozs. nitrite (97 per cent.) dissolved in about $2\frac{1}{2}$ gals. of water. The diazo solution should be perfectly clear in about ten minutes. The temperature during the process should be 46°–50° F.

Helio Fast Red Lakes

The dye-stuff is supplied in the form of 25 per cent. paste and in powder in those cases where the lake manufacturer prefers not to make up the dye from the intermediates.

To produce the lake, all that is necessary is to add from 5 per cent. to 10 per cent. of the dried dye-stuff to blanc-fixe, Paris white, or other suitable base, and run for half an hour under the edge runners ; or alternatively add the 25 per cent. to the base pulped in hot water ; stir well ; filter press ; dry ; runner under the edge runners and sieve.

Properties.—The resultant lake is of a yellowish red tone (scarlet) and of an excellent degree of fastness to light and lime, far superior to Lithol red R or Lake red P. Hence they are largely used in the manufacture of permanent red paints and enamels, distempers, etc.

They will withstand a temperature of 150° F. without change of colour, and consequently are excellent for stoving reds.

Lithol Red R (Badische), Monolite Red R (B.D.C.)

Lithol red R is one of the most widely used and important dye-stuffs in the lake industry. It comes into the market in the form of a 20 per cent. or 25 per cent. paste as the sodium salt.

Constitution.—2-naphthalymine-sulpho acid + B-naphthol.

Lithol Red Lake

This lake is made as follows :—

Blanc-fixe or barytes	100 lbs.
25 per cent. lithol red R paste	40 „
1 : 10 barium chloride	10 „

The base is mixed with ten times its weight of water, and the paste dye-stuff washed in through a sieve with water. The stirrers are set going and steam passed in. A 10 per cent. solution of barium chloride is then gradually run in until complete precipitation is effected. The lake is just brought to the boil so that it froths up well, then the steam is shut off.

The lake is well washed to remove all soluble salts, filter pressed, and dried. The dried lake is runnered for fifteen minutes to develop the shade.

If the barium chloride is replaced with calcium chloride a much bluer shade is produced.

According to the Badische Patent D.R.P. 175630, a lake may be made as follows :—

Barytes	100 lbs.
Lithol red R paste (25 per cent.)	20 „
Barium chloride or calcium chloride (saturated solution in water)	2½ „

The paste dye-stuff is mixed with the barytes and runnered, gradually sprinkling in the saturated solution of barium chloride. The paste is dried, then runnered again to develop the shade. The author has tested this method out, and has found it to give excellent results.

Properties of the Lithol Lakes.—The barium lake is of a bluish-red shade, with a deep blue red undertone ; as calcium lake a still bluer shade is obtained.

The lakes are of fair fastness to light, much superior to the old Ponceau lakes, but not so fast as the Helio Fast Reds. They are fast to water and lime, and are not soluble in spirit or oil (non-bleeding). They possess excellent covering power, and are of good stability to heat.

CRIMSON AND CLARET LAKES

Lake Bordeaux B Paste (Meister Lucius & Bruning)

Constitution.—Naphthylamine-sulpho acid + B-oxynaphthoic acid.

Properties.—These lakes are prepared according to the method used for Lithol red R, using calcium chloride, and give a rich crimson or claret colour of good fastness to light and lime.

The range of this class of dye-stuffs is so large that it is impossible, within the scope of this work, to give a fuller account of the varieties placed on the market under such names as Pigment Red 2 B, 4 B, 6 B (Berlin), Lithol Rubine 3 B, G (B.A.S.F.),

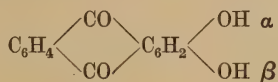
Lake Red D (M), Helio Purpurine 3 B L, Lake Red P (Meister), etc. For fuller description the reader should refer to special works dealing with the synthetic coal tar industry (see Bibliography).

E. MORDANT OR ADJECTIVE DYE-STUFFS

The chief representative of this important group of colours is alizarine red, which, owing to its exceeding fastness to light, is very largely used in the manufacture of permanent lake reds. Besides alizarine red there is also alizarine blue, alizarine heliotrope, alizarine delphinol, alizarine brown, alizarine orange, etc., which are used to a lesser extent by the lake manufacturer.

Alizarine (the colouring matter of the madder root) was first prepared artificially by Perkin, and Graebe & Liebermann, in 1868, and is now manufactured in enormous quantities from anthracene by a modification of their original process.

The constitution of alizarine is—



Alizarine Lakes

The dye-stuff comes on to the market in the form of 20 per cent. red paste, and the following example will illustrate how this lake is produced on the large scale :—

Example

Alizarine 1 B	25 lbs.
Phosphate of soda	1 : 20	34 „
Soda ash	1 : 10	5 „
Turkey red oil	1 : 10	12 „
Alum	1 : 20	50 „
Lime	1 : 30					

Method.—Mix the alizarine paste with 25 times its weight of hot water ; add the weak soda phosphate solution (20 per cent.), then the solution of soda ash, stirring continuously. The alizarine becomes dissolved ; then add the Turkey red oil solution previously neutralised with ammonia.

Next gradually run in the weak alum solution, and continue stirring during the remainder of the process.

Frothing takes place at this stage owing to the evolution of carbon dioxide. Finally add the freshly slaked lime solution, care being taken to run through a fine sieve to remove any grit that may be present.

Steam is now passed in and the whole raised to the boil and boiled for three hours till the colour is fully developed. It is important to see that there is no iron in the chemicals used or in any part of the vat which comes in contact with the lake, as the beauty of the alizarine lake would be thereby destroyed. Wash well, filter press, and dry.

To reduce this lake 120 lbs. of blanc-fixe paste may be added.

In the author's opinion the finest shades of alizarine lakes are obtained by steaming under pressure, using rather more neutral Turkey red oil than given in the above formula.

Properties.—The alizarine lakes are of the utmost value in the paint enamel and printing-ink trades on account of the brilliance and beauty of their shades and their great permanency.

Their shades are of a rich deep bluish colour, which are quite fast to lime and are unaffected by oil or spirit.

F. LAKES FROM INSOLUBLE PIGMENT DYE-STUFFS

In this class are included the more recently introduced insoluble dye-stuffs which have been put on the market by the various German dye factories. They are especially remarkable on account of their fastness, and as they are quite insoluble in water their method of formation into lakes or pigment colours simply consists in mixing up the paste with the base and drying out. Or, in the case of the dry dye-stuffs in adding the colour to the base under the edge runner.

As an example of this class of dye-stuffs we may mention—*Bayer*, Hansa Yellow 5 G, Helio Chrome Yellow 28227, Helio Chrome Yellow G L, Helio Fast Yellow 6 G L, Helio Fast Pink R L, Algole Blue 3 R, Helio Orange C A G, Pigment Chlorine G G, Thio Indigo, etc. The undermentioned examples will illustrate the preparation of lakes from these pigment dye-stuffs:—

Example 1.

Barytes	.	.	.	120 lbs.
Zinc oxide	.	.	.	60 „
Helio Fast Pink R L	.	.	.	1 „

Example 2.

Blanc-fixe	.	.	.	100 lbs.
Hansa yellow paste	.	.	.	50 „

Example 3.

Barytes	.	.	.	50 lbs.
Orange lead	.	.	.	50 „
Helio Orange C A G	.	.	.	5 „

Example 4.

Barytes	.	.	.	60 lbs.
Permanent red 4 R extra	.	.	.	15 „
Zinc oxide	.	.	.	25 „

Every year new insoluble dye-stuffs are being put on the market, and it is only a question of time when the lake manufacturer will have a range of dye-stuffs at his disposal equal in fastness to the inorganic colours, and be able to dispel the erroneous idea still held by many that all dye-stuff colours are necessarily fugitive.

SCHEME FOR THE ANALYSIS OF LAKE PIGMENTS

The analysis of lakes and lake pigments may be conveniently divided in the following manner:—

1. The analysis of the base or “carrier.”
2. The identification of the dye-stuff—or several dye-stuffs, as the case may be—which have been used in their production.

The analysis of the base or carrier is a comparatively simple matter, as the number of inert materials used for this purpose is limited, and the usual methods of inorganic analysis will readily identify them.

The identification, on the other hand, of the dye-stuff or dye-stuffs that have been used in the production of a lake is one that presents very great difficulties, not only on account of the large number of dye-stuffs that are now employed, but also because the process used in the precipitation of several dye-stuffs on one base (such as in the preparation of combined or "mixed" lakes) tends to mask the reactions, and thus prevent their ready determination.

We will now briefly indicate the methods in use for the analysis of lakes and lake pigments.

Physical Tests

A preliminary examination of a lake as regards its physical characteristics will often give valuable indications as to its composition, and should always be carried out.

If, for example, a small portion of the lake be rubbed up on a white palette in oil, its texture will indicate generally the nature of its base, and will serve to identify it.

Alumina bases, for instance, yield tough transparent lakes, which are hard to grind out, while blanc-fixé bases, on the other hand, are extremely soft in texture, and have moderate body and covering power. Barytes bases are readily identified by their peculiar, harsh, gritty texture, however fine the barytes used may be.

The colour of the lake in oil, and its undertone, should be carefully noted, as this often gives a clue by means of which the dye-stuff precipitated on the base may be readily ascertained. For example, Lithol lakes give in oil deep blue undertones, while Para reds give slight brown or colourless undertones.

Analysis of the Base or Carrier

Take 2 gms. of the lake, and gently ignite in a crucible till all the dye-stuffs are burnt off. The residue left is generally white. Weigh the residue. Treat it with boiling hydrochloric acid; filter and wash well. Test residue for barytes by the flame test.

The filtrate is tested for alumina, zinc oxide, and so on, and, if required, the amounts present may be estimated in the usual manner.

The bases in most common use are barytes, blanc-fixe, alumina, alumina blanc-fixe, green earth, whiting and terra alba. Red and orange lead, zinc oxide, and white lead are also used in addition to give body to a lake, and also to tone up the colour.

The Identification of the Dye-stuffs

The identification of the dye-stuffs in a lake is a very tedious operation, except in those cases where the lake contains only one simple dye-stuff, which gives characteristic tests by which it may be readily recognised, such as the eosines, alizarines, and so on.

THE REACTION OF VARIOUS REAGENTS ON SOME OF THE MORE IMPORTANT ANILINE LAKES

Lake.	(1) Alcohol.	(2) Alcohol Potash.	(3) Hydrochloric Acid.	(4) Sulphuric Acid.	(5) SnCl ₄ +HCl.
Eosine . . .	Reddish fluorescent solution	Deep reddish fluorescent solution	Yellowish solution	Yellowish solution	Pale yellow solution
Scarlet 2 R . .	Yellowish-red solution	Brownish-red solution	Brownish solution	Brown scarlet solution	Decolorised
Ponceau . . .	Faint reddish solution	Deep red solution	Faint red solution	Deep red solution	Decolorised
Paranitraniline red	Faint yellowish solution	Brownish-red solution	Dark red solution	Purple red solution	Unchanged
Ortho-anisidine .	Insoluble	Reddish-purple solution	Dark purple red	Dark purple red	Slowly discharged
Alizarine . . .	Insoluble	Light violet solution	Dirty brown solution	Dirty brown solution	Pale yellow
Lithol red R . .	Insoluble	Blue violet solution	No change	Reddish violet solution	Slowly discharged
Lake red P . . .	Slightly soluble	Deep bluish	Slight effect	Reddish violet	Pale yellow
Helo fast red . .	Insoluble	Reddish solution	Slight effect	Pale blue solution	Slowly discharged
Methylene blue . .	Blue solution	Deep blue solution	Bluish-green solution	Green solution	Decolorised
Naphthol green B .	Insoluble	Deep greenish solution. Turns black	Green solution	Brownish solution	Slowly decolorised
Malachite green . .	Deep green solution	Deep green solution	Yellowish solution	Deep orange	Decolorised
Hansa yellow . . .	Insoluble . . .	Deep yellow solution	Deep yellow solution	Orange solution	Turns pale yellow
Auramine . . .	Yellow solution	Deep yellow solution	Yellowish solution	Brownish solution	Discharged

The usual method of procedure is to treat the lake with various reagents, and note its behaviour under such treatment. This is carried out in the following way:—

A portion of the lake is boiled up in a test tube with (1) water, (2) alcohol, (3) alcoholic potash, (4) freshly distilled aniline, (5) sulphuric acid, (6) hydrochloric acid, (7) stannous chloride solution+hydrochloric acid, (8) acetic acid.

The colour of the dye-stuff obtained on filtration is carefully noted.

The table on page 148 gives the reactions obtained with some of the lakes which are in common use in the paint and printing-ink trades. (For a more detailed account the reader is referred to special works dealing with the subject, such as Schultz and Julius, "A Systematic Survey of the Organic Colouring Matters," or George Zerr, "Bestimmung von Teerfarbstoffen in Farblacken.")

The identification of the dye-stuffs present in a given lake by means of the reagents given above is very much facilitated by repeating the tests on known standards. For this purpose standards are previously prepared of all the dye-stuffs which are in common use in the manufacture of lakes by precipitating 5 and 10 per cent. respectively of the dye-stuff on to (1) an alumina, (2) blanc-fixé, and (3) barytes base. By this means is obtained a large range of lakes containing a definite and known percentage of given dye-stuffs on which tests with different reagents can be carried out.

Thus, for example, if a given lake is identified as being a Lithol red on blanc-fixé, then the tests can be repeated on the 5 and 10 per cent. Lithol red lake standards previously prepared, and so checked. In addition to this the strength of the lake can also be determined by a comparative strength test against these standards.

If the above tests be carefully and systematically carried out, it will be possible, after some experience, to identify not only the dye-stuffs present in any body, but, also the amount, and by this means to make up similar lakes having identical properties and shades.

The following coal tar colouring matters, manufactured by the British Dye-stuff Corporation (1922), are specially suitable for the manufacture of lake colours.

All the dye-stuffs mentioned are readily soluble in water, except—

Monolite Red R	=	Badische Lithol Red
„ Fast Scarlet R	=	„ Fast Scarlet R
„ Red P	=	„ Lake Red P

The table appended shows the fastness of these lakes as regards light, spirit and water:—

SOLUBLE COLOURS

No.		Fastness to		
		Light.	Water.	Spirit.
1	Chrysophenine G . . .	Good	Insoluble	Soluble
2	Naphthol Yellow F Y . . .	Very good	Slightly soluble	Insoluble
3	Acid Yellow 85539 . . .	Very good	Insoluble	Insoluble
4	Citronine Y Concentrated . . .	Fair—good	Slightly soluble	Soluble
5	Metanil Yellow Y . . .	Poor—fair	Slightly soluble	Soluble
6	Metanil Yellow W M . . .	Poor	Slightly soluble	Soluble
7	Acid Orange G . . .	Poor	Insoluble	Soluble
8	Coomassie Milling Scarlet G . . .	Poor	Insoluble	Slightly soluble
9	Acid Scarlet R . . .	Poor	Insoluble	Slightly soluble
10	Ponceau R G . . .	Poor	Insoluble	Slightly soluble
11	Scarlet 81024 . . .	Poor	Insoluble	Insoluble
12	Acid Scarlet 3 R . . .	Poor	Insoluble	Slightly soluble
13	Milling Scarlet 5 B . . .	Poor	Insoluble	Soluble
14	Eosine Y S . . .	Poor	Slightly soluble	Soluble
15	Lake Scarlet 3 B . . .	Very good	Insoluble	Insoluble
16	Chlorazol Fast Pink B K . . .	Very good	Insoluble	Insoluble
17	Azo Geranine B . . .	Fair	Insoluble	Insoluble
18	Pure Bordeaux B . . .	Poor	Soluble	Soluble
19	Fast Acid Blue R H . . .	Good	Insoluble	Insoluble
20	Coomassie Violet R . . .	Poor	Insoluble	Soluble
21	Soluble Blue 3 M . . .	Fair	Insoluble	Soluble [extent
22	Pure Soluble Blue . . .	Fair	Insoluble	Soluble to some
23	Alkali Blue 4 B . . .	Fair	Insoluble	Soluble
24	Induline 5 B . . .	Good	Insoluble	Soluble
25	Durasol Acid Blue B . . .	Very good	Insoluble	Insoluble
26	Disulphine Blue A . . .	Poor	Insoluble	Slightly soluble
27	Acid Green G . . .	Poor	Insoluble	Soluble
28	Naphthol Green B 9211 K . . .	Excellent	Insoluble	Insoluble
29	Nigrosine G Crystals . . .	Good	Insoluble	Soluble
30	Chlorazol Black F F X . . .	Good	Insoluble	Soluble
31	Auramine O . . .	Poor	Soluble	Soluble
32	Chrysoidine Y R P . . .	Fair	Soluble	Soluble
33	Bismarck Brown G . . .	Fair	Soluble	Soluble
34	Bismarck Brown R 100's . . .	Fair	Slightly soluble	Soluble
35	Safranine T. Concentrated . . .	Poor	Soluble	Soluble
36	Tannin Pink C . . .	Poor	Soluble	Soluble
37	Magenta Large Crystals . . .	Poor	Soluble	Soluble
38	Magenta 2 B Powder . . .	Poor	Soluble	Soluble
39	Methyl Violet 2 B Conc. . .	Poor	Soluble	Soluble
40	Methyl Violet 10 B L . . .	Poor	Soluble	Soluble
41	Indine Blue 2 R D . . .	Very good	Soluble	Soluble
42	Methylene Blue G S . . .	Very good	Soluble	Soluble
43	Turquoise Blue G . . .	Poor	Soluble	Soluble
44	Malachite Green Crystals A Con- centrated . . .	Poor	Soluble	Soluble
45	Brilliant Green Crystals Y . . .	Poor	Soluble	Soluble

INSOLUBLE COLOURS

No.		Fastness to		
		Light.	Water.	Spirit.
46	Monolite Fast Scarlet R paste . . .	Excellent	Insoluble	Insoluble
47	Monolite Red P paste . . .	Very good	Insoluble	Soluble
48	Monolite Red R paste . . .	Fair	Insoluble	Soluble

CHAPTER XIV

THE ANALYSIS AND EVALUATION OF PIGMENTS ACCORDING TO THEIR PHYSICAL PROPERTIES

THE chemical analysis of the various pigments has already been indicated under their respective headings in the previous chapters dealing with their manufacture and properties.

It is desirable, however, to give also a brief account of the general physical tests which should be applied to pigments in order to determine their suitability and properties when used in the manufacture of paints.

The chief physical properties of pigments which should be considered in this connection may be briefly enumerated as follows :—

1. Specific gravity.
2. Fineness.
3. Colour, brightness and cleanness of tone.
4. Oil absorption.
5. Strength.
6. Hiding power.
7. Covering power.
8. Permanency.

1. SPECIFIC GRAVITY

The specific gravity of a pigment may be determined by any of the well-known physical methods. The specific gravity bottle is especially suitable for the purpose, and the determination is carried out in the following manner :—

A 50 gm. bottle (Fig. 21) is weighed. The weight of distilled water at 15.5° C. which the bottle contains is ascertained. The pigment is now introduced into the dry bottle, the whole is weighed, and the weight of the pigment is obtained by difference.

The bottle containing the solid is now filled with distilled water; air bubbles enclosed in the pigment are removed by heating or shaking; the liquid is brought to the temperature of 15.5° C.; additional water is added if necessary to fill the bottle quite full; then the stopper is inserted and the excess water

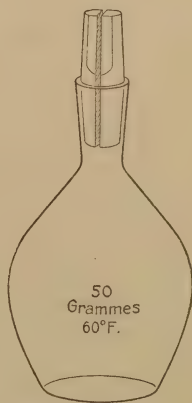


FIG. 21.—SPECIFIC GRAVITY BOTTLE.

oozing out is carefully wiped away, and the bottle and its contents are weighed again.

The ratio of the weight of the pigment to the weight of water displaced by it is the specific gravity of the pigment.

Average Specific Gravity of some of the Common Pigments

Basic carbonate white lead	6.81	Litharge	8.81
Basic sulphate white lead	6.41	Purple oxide	5.34
Normal lead sulphate	6.08	J.F.L.S. yellow ochre	2.95
Zinc oxide	5.66	Raw sienna	5.32
Lithopone	4.30	Raw umber	4.52
Barytes	4.46	Pale chrome yellow	5.89
Blanc-fixe	4.28	Pale chrome green	5.73
Terra alba	2.34	Zinc chrome	3.69
Paris white	2.61	Prussian blue	1.97
Precipitated chalk	2.56	Ultramarine blue	2.50
China clay	2.65	Vegetable black	1.72
Asbestine	2.75	Graphite	2.46
Silica	2.60	Bone black	2.35
Red lead	8.68	Venetian red	5.23
Titanium white	4.00	Vermilion	6.83

2. FINENESS

The testing of a pigment as regards its fineness is of the utmost importance for many reasons. In the first place a certain degree of fineness is obviously necessary before the mixture of solid substances and oil can be uniformly spread over a surface with a brush, as very coarse particles will naturally settle out quickly from the oil. Paints made up from coarse pigments will dry off with a rough and displeasing surface or finish.

Further, the fact must not be lost sight of that the hiding power of a pigment is inversely proportional to the diameter of the particles, or, in other words, the smaller the particles the greater the hiding power.

In addition, the finer the particles of a given pigment, when mixed to a painting consistency in a given medium, the greater the covering or spreading power of that pigment.

The rough and ready test which is usually applied to a pigment to determine its fineness is carried out in the following way:—

A small portion of the pigment is spread on a white porcelain palette and rubbed with a palette knife—(1) in the dry state, (2) with oil, (3) with turpentine. By this means a general idea will be obtained as to its texture and degree of fineness as compared with a standard sample of known fineness.

The comparative fineness of a pigment may also be ascertained by noting the time required for 5 gms. of the pigment, when shaken up in a cylinder filled with

petroleum ether (or other liquid of low specific gravity) to settle out as contrasted with other pigments of the same type.

The quantitative estimation of the amount of coarse particles in a pigment may be determined by sieving the material through a series of fine sieves and silk bolting cloths, and weighing the various residues, or by means of the Elutriator (see Chapter VI.).

The best means for separating and estimating pigments according to size is by the Thompson Classifier, a description of which is given in the "Proceedings of the American Society for Testing Materials," vol. x., 1910.

3. COLOUR

A coloured object, not self-luminous, owes its colour to the fact that it absorbs some colours of the light which falls on it, reflecting and scattering the rest. Thus blue paint absorbs red and yellow, reflecting only green, blue and violet. Yellow paint absorbs all but red, yellow and green. Hence when blue and yellow paints are mixed, the only colour which is not absorbed is green, which is reflected both by the blue and the yellow pigments.

The colour of a given pigment is always ascertained by comparison with other standard colours of a similar type.

Thus the purity of the colour of a white pigment is determined by comparison with other white pigments, both in their dry state and when ground in a colourless medium such as bleached poppy seed oil.

The colour may be described as being a dirty white, or of a bluish shade, yellowish tone, greyish tint or tone, and so on, according to the colour tone which it possesses.

Coloured pigments are likewise classified by comparison with other pigments of a similar shade, and careful note should be taken of their brightness and cleanness of shade, depth of colour, and of their undertone and overtone.

For example, two Prussian blues compared side by side may show considerable differences; one may be of a bright clean tone, with a violet shade and bronzy lustre, while the other may be of a dirty greenish shade and devoid of any bronzy appearance.

The Tintometer

Attempts have been made to construct an instrument by means of which records of colours may be accurately registered. The Lovibond Tintometer (Fig. 22) is by far the best instrument of this class, and by its use it is possible to determine the colour and tint of all materials used in decorative work.

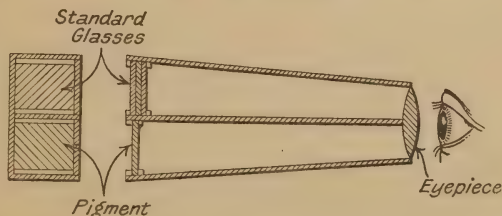


FIG. 22.—THE LOVIBOND TINTOMETER.

The instrument consists of a double tube ending in an eyepiece at the smaller end. At the other end are equal apertures for viewing the colour to be measured alongside of standard glasses.

To apply the instrument for colour measurements there is provided a set of standard coloured glasses, which can be placed in suitable grooves at one side of the wider end of the double tube, while on the other side is put the colour which is to be measured.

One or more of the standard colour glasses are put into the tube until the colour and tint of the pigment is exactly matched. A note of the numbers of the glasses thus records the matched colour.

Over 400 standard coloured glasses are supplied, coloured in various degrees of intensity and in even gradations.

4. OIL ABSORPTION

The oil absorption or oil-carrying capacity of a pigment is, for practical purposes, the amount of oil required to grind a pigment into a stiff paste. As is well known, the greater the pressure the less the amount of oil required to convert the pigment into paste form. The oil absorption of a pigment as compared with that of other pigments is usually determined approximately as follows:—5 gms. of the pigments are weighed out on to a palette, and linseed oil is added drop by drop until the pigments when rubbed up hard under the palette knife are converted into a stiff paste.

The number of c.c. of oil required is noted and the result expressed as the number of gms. of oil required to grind 100 gms. of pigment into a stiff paste form. The oil absorption test is of considerable value in the manufacture of colours ground in oil which are sold by weight, as usually the cost of the oil is a good deal greater than that of the pigment.

Thus, for example, in the case of two ochres of similar colour, tone, etc., it is obviously more economical to select the one that requires the lesser amount of oil to convert it into paste form. As a general rule the heavier the pigment the less oil it absorbs.

Approximate Oil Absorption of Various Pigments

	<i>Linseed Oil (by weight).</i>	
White lead (Dutch process)	7	per cent.
White lead (chamber process)	8	„
Zinc oxide	20	„
Lithopone	15	„
Barytes	8.5	„
Whiting	22	„
J.F.L.S. ochre	35	„
Turkey umber	40	„
Vandyke brown	75	„
Vegetable black	90	„

	<i>Linseed Oil (by weight).</i>				
Lemon chrome	14 per cent.
Ultramarine blue	28 "
Prussian blue	75 "
Brunswick green	16 "
Titanium oxide	17 "

5. STRENGTH

The strength test of a pigment is of the utmost importance in its valuation. The pigments should always be compared with carefully selected standards of a similar type in the following manner:—

White Pigments—Zinc Oxide, White Lead, Lithopone, etc.

Weigh out carefully 1 gm. of the white pigment under test on to a white porcelain palette, and add 0.1 gm. of standard Prussian blue. Then add sufficient bleached linseed oil drop by drop from a dropping bottle till the pigments on thorough grinding are converted into a stiff paste form, and the blue is intimately mixed with the white pigment. Note the number of drops of oil used. Repeat in precisely the same manner with a standard sample of zinc oxide, or, if preferred, with a standard white of the same composition as the one under examination. Transfer the tints thus prepared to a microscope slide (Fig. 23), and spread out evenly side by side till they are just touching one another.

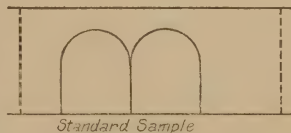


FIG. 23.—MICROSCOPE SLIDE WITH REDUCTION TEST.

Compare the tints thus obtained on both sides of the glass.

If the standard be bluer than the sample under test then obviously it is weaker than the sample, and vice versa.

Sometimes standard ultramarine blue is used in place of Prussian blue in the proportions of white 20 parts to ultramarine blue 5 parts.

Red Colours—Red Oxides, Aniline Reds, etc.

Use 0.1 gm. of the sample to 1 gm. of standard zinc oxide, or 0.25 of colour to 1 gm. of standard white lead.

Greens, Blues and Blacks

Take 0.01 gm. of the sample to 2 gms. of standard zinc oxide.

Chromes (all except Orange)

Take 1 gm. of the sample to 0.25 gms. of standard Brunswick blue (10 per cent. Prussian blue on barytes).

Orange Chrome

Take 0.1 gm. of the sample to 1 gm. of standard zinc oxide.

6. HIDING POWER

The hiding or obscuring power (often called body) of a pigment when made into paint form is the property it possesses of obliterating or masking the surface over which it is spread. This varies inversely as the diameter of the particles, or, to put it in other words, the smaller the particles the greater the obscuring power.

In the case of a white pigment the obscuring power is the function of its capacity for reflecting light. The amount of reflected light depends closely upon the number of reflections from a pigment film of a given thickness and on the size of the particles in the pigment film.

The hiding power of a pigment must not be confused with its covering power. Thus while two coats of white lead paint are about equal in opacity or hiding power to three coats of zinc oxide, the covering power of the latter is, as is well known, considerably greater than white lead.

Lakes prepared by precipitating dye-stuffs on an alumina base are known as transparent colours, and although they may cover well, they are deficient as regards body.

The determination of the hiding power of pigments is usually carried out in the following manner:—A white board traversed with black lines is carefully divided into equal areas. The pigments to be tested for opacity or body are ground up in raw linseed oil to a stiff paste form, careful note being taken of the amount of oil used. A weighed-out quantity of these stiff pastes is thinned down to brush consistency with a standard paint medium consisting of 10 parts of pale boiled oil, 2 parts of turpentine, and 1 part of pale terebine.

The prepared paints are weighed out into tins each provided with a small brush. The paints are then brushed on to the equal divisions of the board as thinly and evenly as possible, a sufficient number of coats being applied till the black is completely obliterated in each case. As a rule two coats will suffice, except where the body of the paint is very poor, when more coats will be necessary.

Each tin with brush is then weighed after this operation in order to ascertain the weight used. It is then easy to calculate the relative opacities of the pigments under test.

A large number of tests should be made so as to get a fair average result and to reduce the error caused by the laying on of any excess of paint over the minimum required to produce complete obliteration.

Spray Test

The author has obtained exceedingly good relative results by breaking the paints down to spraying consistency and spraying them on to a given area of doped fabric—the weight of which is known—until complete obliteration has taken place. The fabric is again weighed after the paint has dried on.

This process was found to give much more uniform results than could be obtained by the brush method, due doubtless to the elimination of the personal error. Moreover, much thinner and more uniform coats of paint can be applied by spraying than is possible by the brush method.

Dr Pfund has invented a very simple instrument called the "cryptometer"¹ for determining the true numerical values of the obscuring powers of pigments and paints.

7. COVERING POWER

The covering or spreading power of a pigment is measured by the greatest area over which unit mass of a pigment mixed to a painting consistency with a given medium can be uniformly spread with a brush.

As a rule two pigments in an equally fine state of subdivision will show spreading powers inversely proportional to their specific gravities.

The covering power of pigments is usually determined by the relative areas covered by 100 gms. of the pigments when reduced to paint consistency. The following method is usually adopted for determining the covering power of pigments:—

The pigments are made up into paint form as described in paragraph 6 and brushed on to primed boards, care being taken to spread the paints as thinly and uniformly as possible.

The area covered by a known weight of the paint is then measured and the result expressed either as the number of square feet covered by 100 lbs. of the pigment, or more usually the number of square feet covered by 1 gallon of the paint.

The following table gives some of the physical data obtained by practical tests on zinc oxide, white lead and lithopone:—

	<i>Zinc Oxide.</i>	<i>White Lead.</i>	<i>Lithopone.</i> (30 per cent.)
Specific gravity . . .	5.66	6.81	4.30
Oil absorption . . .	20	8	15
Relative strength . . .	100	57	70
Relative hiding power . .	100	156	120
Relative covering power .	100	62	69

8. PERMANENCY

In addition to the various physical properties of pigments which have already been discussed, there are others which require to be carefully considered in estimating the value of a pigment as a paint material, chief of which are durability and colour, stability on exposure to sunlight, and weathering influences.

The simplest method of testing the permanency of a pigment is to make it up into paint form and brush one or two coats on to wood and iron and expose to the atmosphere.

A portion of the painted surface is covered with a strip of wood to protect it

¹ *Farben Zeitung*, Jan. 1920.

so that comparisons can be made later on between the exposed and protected surfaces.

The paint should be washed down from time to time, and the results of the weathering influences noted as regards (1) change of colour, (2) cracking, and (3) chalking. In this way an estimate may be formed as to its durability and colour stability as compared with the portion protected from exposure.

The permanency of pigments to light may also be tested by grinding them up in gum arabic solution and painting them on to a piece of non-absorbent paper in strips side by side. The paper is hung up inside against a window exposed to as much sunlight as possible, care being taken to protect a portion of the painted paper from the light by means of a strip of black paper which may easily be removed from time to time so that a comparison may be made as to the effect of the light on the various colours.

A quick test for determining the colour stability of pigments may be made by exposing paint films on glass to the rays from the mercury lamp.

The results of exposure tests on the commonly used white pigments that are made up into paints indicate that white lead, while it has the defect of tending to turn slightly brown, especially on exposure to town atmospheres, possesses remarkable properties as regards durability and stability under the most severe weathering conditions, and is far superior in its protective qualities to any other white pigment in common use.

Zinc oxide, titanium oxide, and antimony oxide retain their colour extremely well for a time, but after exposure for a period over twelve to eighteen months they tend to show chalking effects.

Lithopone¹ paints, on the other hand, readily discolour, turning grey, and after a few months' exposure commence to chalk and shell off; hence they are of little value as protective paints for outdoor use.

The natural earth colours such as the ochres, umbers, red oxides, etc., are extraordinarily permanent, and retain their colour even after long exposure to the most severe conditions.

Brunswick greens, chromes, Prussian blues, and other similar manufactured colours are as a rule moderately permanent. Ultramarine blue and vermilion are, however, very permanent colours.

Aniline lakes show remarkable differences as regards their colour stability, *e.g.* alizarine, helio fast rubine R L, helio chrome yellow G L, lakes, etc., exhibit striking permanency to light, while other lakes, such as those made from eosine, magenta, methyl violet, etc., are very fugitive, and lose their colour completely after only a few weeks' exposure.

The permanency of a colour when exposed to sulphuretted hydrogen and acid fumes should also be considered; their stability or fastness to lime and alkalies is also of great importance when intended for use in the manufacture of distempers and calsomines (Lime Fast Colours, see Chapter XIII.).

The action of pigments on one another, and on the oil or varnish medium in

¹ Certain brands of lithopone are now manufactured which are fast to sunlight (see Chapter VI.).

which they are ground when made up into paint form, should also be tested to determine whether they are inert to one another or whether there is any action between them.

Some pigments, for example zinc oxide, when ground in acid varnish mediums, such as rosin or Congo copal varnishes, in the preparation of enamels, tend to "feed" or thicken up.

White lead, as is well known, tends to form a lead soap when ground in linseed oil, and to this fact may be ascribed in a large measure the remarkable elasticity and durability of lead paints; titanium oxide and antimony oxides, on the other hand, are inert pigments, and have no influence on the medium in which they are ground.

Pigments containing sulphur when mixed with lead pigments are liable to cause discoloration, and on this account such mixtures should be avoided.

Pigments used in the pottery trades must be capable of withstanding high temperatures, hence only pigments such as cobalt oxide, tin oxide, green oxide, chromium, ultramarine blue can be used.

Colours that are soluble in water, *e.g.* calcium chromate, etc., also those that possess toxic properties and are unstable to light, such as emerald green, are unsuitable for general use as pigments in the manufacture of paints or protective coverings.

PART III

Varnishes, Lacquers and Japans

CHAPTER XV

INTRODUCTION, COLOPHONY, SOFT RESINS, BALSAMS AND FOSSIL GUMS

INTRODUCTION

VARNISHES and lacquers may be defined as solutions of various natural balsams, resins, lacs or fossil gums dissolved in suitable solvents or diluents, with or without the addition of a drying oil such as linseed oil.

They dry, as a rule, when applied in thin films with a hard, tough, lustrous surface or "face."

They are applied to various objects with a view to giving them a pleasing, finished appearance; at the same time they have a utilitarian aim in that they serve to protect the material to which they are applied from external injury.

The art of lacquering has been known to the Chinese, Japanese, and other Asiatic races from a very remote period.

The manufacture of oil varnish from linseed oil and gums is of more recent origin; the earliest record we have of it is from a monk named Theophilus, who published directions for making linseed oil varnish in the twelfth century.

Lacquers and varnishes may be classified under the following two groups:—

(1) Oil varnishes.

(2) Spirit varnishes or lacquers.

Oil varnishes dry through the evaporation of the solvent and the subsequent oxidation of the sticky gum oil residue into hard films, through the absorption of oxygen from the air.

In the case of spirit varnishes the drying action is simply due to the evaporation of the solvent, which leaves a solid residue behind.

RAW MATERIALS

The raw materials used in the manufacture of varnishes and lacquers are mainly as follows:—

1. Colophony (rosin), balsams, soft resins, shellacs and fossil gums; also celluloid, nitro-cellulose, cellulose acetate and synthetic resins.

2. Drying oils, such as linseed oil and wood oil.
3. Solvents and diluents, such as turpentine, alcohol, and other volatile liquids.
4. Dryers, siccatives and terebines.

The various resins used in the manufacture of varnishes will be now briefly described as regards their origin and sources of supply, as well as their chief properties.

For convenience the resins will be classified in two groups :—

1. The soft resins, including the balsams and colophony or rosin, which is by far and away the most important and largely used of all the resins.
2. The hard resins or fossil gums, such as animi, amber, kauri, copal, and so on.

(1) COLOPHONY (ROSIN, COMMON RESIN)

Colophony, known commercially as rosin, which term is to be used in preference to resin as being less likely to be confused with other resins, in the residuum left after the expulsion of the oil of turpentine from the resinous exudation of coniferous trees (Gum Thus).

The molten rosin is run out of the stills into casks in which it solidifies to a vitreous mass.

Rosin is imported in large quantities chiefly from the United States, France and Spain. American rosin, which forms the bulk of our supplies, is derived mainly from the long leaf *Pinus Australis*, and French rosin from *Pinus Maritima*, the composition of the two being somewhat different.

The colour of rosin depends on the manner in which the distillation has been carried out. It varies in colour from "Extra pale" ("W G" window glass) and water white ("W W") to F, G, B, G, and B grade; B grade being nearly black.

Composition

Rosin has been the subject of innumerable chemical investigations over many years, but so difficult have these researches proved that there are still many problems connected with the chemistry of rosin that await solution.

Rosin consists mainly of free acids (abietic acid). Tschirch in 1903 by treating an alcoholic solution of American colophony with alcoholic lead acetate obtained three abietic acids—alpha, beta and gamma. These results were afterwards confirmed by Seidel.

Abietic acid has the formula $C_{20}H_{30}O_2$.

French rosin consists mainly of pimaric acids, which are closely related to the abietic acids.

Pimaric acid exists in both lævo and dextro form, and both give crystalline ammonium salts, whereas those of abietic acid are gelatinous.

The pimaric acids appear to have greater stability than the abietic acids of American colophony.

Rosins are generally supposed to be oxidation products of the terpenes, with which they are associated in the natural terpenes.

Properties and Uses

Colophony or rosin is a brittle solid with a glassy fracture. It has a characteristic odour on gently warming. It softens at about 80° C. and melts at 110–135° C.

Rosin is slightly heavier than water, its specific gravity being 1.067 to 1.081.

It is soluble in alcohol, ether, turpentine, white spirit, and practically all organic solvents, and in oils.

It is saponified by alkalis, which combine with the abietic acid to form the rosin soaps which are so largely used in the soap industry.

When rosin is heated at temperatures above its melting point it yields gaseous products and a distillate of rosin spirit and rosin oil (see Chapter XVI.); but in a current of superheated steam (above 200° C.) it can be distilled without any apparent change. Rosin is extensively used in making varnish.

The Analysis of Rosin

An analysis of rosin is hardly ever called for as it is one of the cheapest resins on the market and hence is not liable to adulteration.

It may be readily detected by the Liebermann-Storch test which is carried out as follows:—

Boil 5 gms. of the material, supposed to contain rosin, with 30 c.c. of acetic anhydride; cool, pipette off the acetic anhydride, and add a drop of sulphuric acid 1.53 specific gravity. If rosin be present, even in traces, a fugitive violet colour will be produced.

The amount of rosin present—*e.g.* in an oil or fat—may be determined by the Twitchell method, which depends on the fact that when dry hydrochloric acid is passed through a solution in absolute alcohol no rosin esters are formed.

Analytical Constants of Commercial Rosin

Specific gravity at 15.5° C.	1.065–1.082
Melting point	150° C.
Acid value	164
Saponification value	175
Iodine value	80–220
Ester value	18
Unsapönifiable	7

The analytical constants given above are only approximate as the figures obtained vary considerably in different varieties of rosin. The iodine value varies to such an extent that it is of no value as a constant for rosin.

HARDENED ROSIN

If rosin be raised to about 200° C., and lime or zinc oxide stirred in, a vigorous reaction takes place owing to the combination of the rosin acids (abietic acid) with the lime or zinc oxides whereby a calcium or zinc resinate is produced.

The melting-point of the rosin is thereby raised and so these resins which are known as "hardened" rosins are used very extensively in the manufacture of hard-drying varnishes.

Varnish made with rosin tends to dry sticky, but with calcium or zinc resinate it dries off hard, and is more durable and withstands atmospheric influences better.

Other metallic resins such as copper, cobalt, lead, manganese, aluminium, and others, are also produced in a similar way to that of the calcium and the zinc resins.

Copper resinate is used in anti-fouling compositions (see Chapter III.), while the resins of lead, manganese and cobalt are largely used as driers (see Chapter XX.).

ROSIN ESTERS OR ROSIN GUMS

A resin ester is made by combining a resin acid with an alcohol, with the elimination of water. Glycerine rosin esters are made by combining rosin with glycerol.

The colophony is melted in large iron pans, or in autoclaves, with about 10 per cent. of its weight of glycerol in the presence of catalytic and dehydrating agents. The glycerol combines with the rosin to form a nearly neutral ester gum.

The rosin glycerine ester gums are largely used in the manufacture of outside varnishes, especially in conjunction with wood oil on account of their superior wearing and weather-resisting properties as compared with the lime-hardened rosins.

Varnishes made with ester gums, on account of their low acidity (A.V. 10-15), do not thicken or liver up with zinc oxide, a property which is of extreme importance in the manufacture of enamels.

Ester gums are insoluble in alcohol, but perfectly soluble in turpentine and white spirit.

BALSAMS

Common Frankincense (Gum Thus., Galipot, Thus. Americanum.)

Crude turpentine, which concretes on the trunks of various coniferous trees, especially in France and North America, was formerly scraped off and used in pharmacy under the generic name of balsam.

The ordinary fresh crude turpentine (Gum Thus.) is a soft pale yellow opaque viscous material (which is intermediate between spirit of turpentine and rosin) with a turpentine-like odour. On keeping, it becomes dry and brittle and darker in colour, and loses its odour.

These natural balsams have a limited use as softening agents to lessen the brittleness of various varnishes and lacquers.

CANADA BALSAM

(Canada Turpentine, Terebinthina Canadensis.)

This balsam is the oleo-resin obtained from *Abies balsamea*, a species of Canadian pine tree.

Properties.—It is of a pale yellow and faintly greenish transparent colour of the consistence of thin honey. It has a peculiar, agreeable aromatic turpentine-like odour, and a slightly bitter acrid taste.

On exposure to the air it slowly dries, giving a transparent film. Its specific gravity is about .998. It is soluble in benzol, ether and alcohol.

BURGUNDY PITCH

(Pix Burgundica.)

The resinous exudation obtained from a species of pine (*Pinus abies*, *Abies excelsor*, *Picea excelsa*) which flourishes in the Vosges and the Alps.

Properties.—It is hard and brittle, yet gradually takes the form of the vessel in which it is kept. It possesses a sweet aromatic turpentine-like odour, especially when heated by the warmth of the hand.

It is readily soluble in glacial acetic acid, ether and spirits of turpentine. It always contains a proportion of water. It is often adulterated largely with colophony.

VENICE TURPENTINE

Venice turpentine is obtained from the common larch (*Pinus larix*) which grows in the Tyrol and in France. It is of a bright greenish-yellow colour, and of the consistency of honey, and does not harden on exposure. On this account it is used as a softening agent in spirit varnishes. It has a sweet aromatic smell like turpentine.

It melts about 110° C., and has a specific gravity of 0.856. It is soluble in most organic solvents, such as alcohol and ether.

SOFT RESINS

The soft resins may be differentiated from the hard copals by their ready fusibility. They vary considerably as regards their hardness from gum elemi, which is of a soft, sticky nature, to Manila copal, which requires a temperature of about 135° C. to melt it.

The soft resins are used mainly in the manufacture of spirit varnishes on account of their ready solubility in alcohol, turpentine and other volatile solvents.

ELEMI

This resin is of a whitish colour when quite pure, with a pleasant aromatic odour. Its specific gravity is about 1.08.

It is obtained from various trees such as *Canarium luzonicum* in Manila, Central, and South America, and the East Indies.

The resin is, as a rule, of a soft and sticky nature, and although, as stated, generally of a whitish colour, some varieties, such as Mexican elemi, are harder and of a pale yellow colour.

Elemi resin softens at about 80° C. and melts at 120° C. When distilled it yields about 10 per cent. of a mixture of volatile oils isomeric with spirits of turpentine.

It is soluble in alcohol, turpentine, and most organic solvents.

It is not used by itself in making varnish, but is added as a toughener or softening agent to spirit varnishes in order to make them less brittle and more elastic.

GUM BENZOIN

Gum benzoin or "gum benjamin" is the aromatic resin of the styrax benzoin, a tree which is native of Sumatra, Java, the Malay Peninsula, and Siam.

Commercially two forms of the gum are used—one from Sumatra and the other, which is more highly esteemed, from Siam.

The natives make excisions in the trees, and after about a fortnight the resin flows freely and is collected.

Benzoin usually appears on the market in brownish coloured lumps, containing opaque yellowish white tears or almonds, with a good deal of debris of bark and wood.

When warmed it gives off a strong characteristic sweet vanilla-like odour. It melts at about 100° C.

It is soluble in alcohol (all except the impurities); in ether, turpentine, and white spirit it is only partially soluble.

It is composed of resinous bodies, benzoic acid and a little cinnamic acid. On gently heating it melts, giving off clouds of white fumes of benzoic acid. Its specific gravity is about 1.14.

Benzoin is used in spirit varnishes to impart a fragrant odour and also to improve and harden the gloss.

MASTIC

Mastic is chiefly obtained from the island of Chios, one of the principal islands of the Greek archipelago, and is the product of the lentix tree (*Pistacia lentioscus* L.).

Vertical incisions are made in the bark of the tree from which the liquid resin trickles, and soon becomes dry and hard.

Mastic comes on to the market chiefly in the form of spherical or tear-shaped grains. It is of a pale yellow colour, inclining to green; it is very brittle, but softens in the mouth after long chewing, and is used in Turkey as a chewing gum.

Its specific gravity is about 1.05. It melts at about 108° C., but softens at about 85° C.

Mastic contains a resinous acid (mastic acid, $C_{40}H_{64}O_4$), and is soluble in turpentine, alcohol, acetone, but not in petroleum spirit.

It is used in making varnish for the use of artists. Mastic varnish mixed with boiled oil forms a gelatinous mass known as "megilp," which is also employed by artists in oil painting. "Gumption," which is used for a like purpose, is made by mixing mastic varnish with a little linseed oil and sugar of lead.

SANDARAC

This resin, which is also known as gum juniper, is obtained from a species of cypress (*Callitris quadrivalis*) indigenous to North Africa. In part it exudes naturally from the trees, but is also obtained by the Moors, who make incisions in the bark of the tree for the purpose of increasing the flow of the sap.

Sandarac comes on to the market in elongated, small brittle tears, having a vitreous fracture, and is of a pale yellowish colour. Its specific gravity is about 1.04. It does not soften on chewing, which distinguishes it from mastic.

It melts at about 140° C. with a characteristic odour. It is soluble in alcohol, acetone and ether, but only slightly soluble in turpentine and benzol.

Sandarac is used in spirit varnishes to impart lustre and hardness.

DAMMAR

Dammar gum is a resin which is imported chiefly from Java, Sumatra, Siam, and Borneo, and is the produce of the Amboyna pine (*Dammara orientalis*). It comes into commerce in lumps, and also in nodules or grains, usually covered with a powdery crust, the interior of which is transparent and clear. It is friable and breaks easily, with a powdery fracture.

The value of dammar gum depends chiefly on its colour, the finest qualities of which are nearly white in colour, or at the most of a transparent faint yellowish colour.

The usual grades of Batavian dammars that come on the market are Best White, E, A to E (mixed grade), and Dammar Dust. The Singapore dammars are softer and yellower, and not equal in quality to the Batavian.

Dammar has a specific gravity of about 1.06. It is a soft resin, and the heat of the hand is sufficient to make it sticky. It begins to melt at 80° C., and is quite limpid at 160° C. On melting it gives off a characteristic balsamic odour, by means of which it may be readily detected.

It is soluble in turpentine, ether, chloroform, and in oil, but only partially soluble in ethyl alcohol. Solutions in turpentine have a milky turbidity, which can be cleared up by adding absolute alcohol.

Dammar gum is very largely used in the varnish industry for making crystal-white paper varnishes, furniture varnishes, and glossy white enamels.

Varnishes made from this gum dry with brilliant hard glossy surfaces. Unfortunately dammar has the defect of being rather friable, so cannot be used for exterior work (see Chapter III.).

Black Dammar

is obtained from India from a species of Canarium tree by burning the foot of the tree and thus causing the resin to exude. It is not used to any extent in this country owing to its colour.

MANILA COPAL

Manila copal is a product of various species of trees (*Agathis alba*) found growing in the Philippine and Malacca islands. It comes into commerce in two varieties known as spirit Manila gum and hard Manila copal.

The spirit Manila gums are the softer varieties of the gum, melting at about 130° C. and being wholly soluble in alcohol. In order to obtain this gum incisions are made in the trees, or else strips of the bark are cut off, and the exuding resin collected by the natives, after which they are sorted out into different grades.

They are largely used in the manufacture of spirit varnishes.

The hard Manila copals are old fossil remains of resins which have exuded from the trees at some bygone period. They are dug up, washed, and scraped ready for the market. Insoluble in alcohol, they do not melt below about 350° C. They are largely used in the manufacture of oil varnishes.

Manila gum varies in colour from pale yellow to a deep brown. Its specific gravity is about 4.06.

On distillation a large amount of frothing takes place with evolution of water and volatile oils, which contain pinene, limonene, and other terpenes, besides formic acid, acetone, and many other bodies. The acid value and the saponification value vary considerably according to the nature of the gum. The average figures are about—acid value 105, saponification value 150.

LAC (SHELLAC)

Lac is a resinous incrustation found on the twigs of many species of Indian trees (*Ficus*). The lac is formed from the sap of the tree by the female of the lac insect (*Coccus lacca*). The insect punctures the bark of the tree and secretes the lac, which is found hardened on the older twigs. Its colour varies from an orange yellow to a dark red.

The principal portion of the lac of commerce is imported from Calcutta. It is sold in the following forms:—

(1) Stick lac, (2) Seed lac, (3) Shellac, (4) Button lac, (5) Garnet lac.

STICK LAC

is the crude product as it comes from the trees, and is mixed with bark and twigs. It is purified by breaking up into small pieces, thus separating the brittle crude lac, and washing with hot water. By this means all the colouring matter is extracted. The residue is dried and constitutes the seed lac of commerce.

Seed lac is chiefly obtained as reddish-yellow grains, which as a rule contain very little colouring matter.

The reddish liquor is evaporated down and sold as “lac dye,” which was formerly supposed to be identical with cochineal. It has, however, been found that the “lac dye” contains a dye called laccainic acid, represented by the formula $C_{16}H_{12}O_8$.

SHELLAC,

which is the principal lac product used in the varnish industry, is obtained from the seed lac by melting it over a fire and pouring out the easily fusible shellac on to revolving cylinders, from which, as it solidifies, it is scraped off in the form of thin brittle leaves. In this manner the more unfusible material and impurities are left behind.

Properties and Uses.—Shellac is sold in various grades, named according to their colour, *e.g.* T N Orange, Fine Pale Orange, Lemon, Ruby, and so on.

Shellac is soluble in cold alcohol, with the exception of some insoluble substances known as shellac-wax; in hot alcohol the wax dissolves, but on cooling it again separates.

Dissolved in alcohol, shellac gives a turbid brownish-orange solution, which constitutes the French polish of commerce so largely used by cabinetmakers and others.

Shellac is only slightly soluble in ether and turpentine. On boiling with weak alkaline solutions it is saponified and dissolves, giving a deep reddish solution, from which the shellac may again be reprecipitated by the addition of an acid.

The specific gravity of shellac is about 1.182.

Shellac is a tough yet brittle material, which is readily fusible (it melts at about 150° C.), and on burning gives off a fragrant characteristic odour. It is often adulterated with rosin, which, however, may readily be detected by the increased acid value and iodine value, as also by the Liebermann-Storch test.

The analytical constants obtained from orange shellac are approximately as follows :—

Analytical Constants of Orange Shellac

Specific gravity at 15.5° C.	1.182
Melting-point	150° C. (softens at 95°)
Acid value	61
Saponification value . .	201
Ester value	140
Iodine value	18
Unsaponifiable	3.5

BLEACHED SHELLAC (WHITE SHELLAC)

As the colour of shellac is objectionable for some varnishes, bleached shellac is used in its place.

Shellac may be bleached in many ways, as, for example, by treatment with bone black, bleaching powder, hypochlorite of soda, sulphur dioxide. The usual process adopted on the commercial scale is as follows :—

Ordinary shellac is dissolved in a weak hot soda solution, and the requisite amount of hypochlorite of soda (made by adding a solution of soda to a solution of bleaching powder) stirred in. After stirring for four hours, the whole is allowed to stand overnight, when a sample is drawn off which should be colourless.

The shellac is precipitated by adding dilute sulphuric acid, after which the precipitate is strained through cloths and well washed till all acid is removed. The white shellac thus obtained is melted under water, and then when quite soft is kneaded so as to give it a silky appearance.

Bleached shellac is sold usually in the form of hanks or bars containing approximately 20 per cent. of water. To rid the shellac of this water as much as possible it is crushed and spread out in the air for a day or two.

White shellac when dried deteriorates on keeping, becoming insoluble in alcohol; hence in making white shellac varnish—for which purpose it is largely used—it should be dissolved as soon after drying as possible.

Bleached shellac dissolves in alcohol, giving a turbid milky solution, due mainly to the wax it contains, but also partially to traces of water which is always present in white shellac however carefully it may be dried.

Button Lac comes on to the market in the form of round flat pieces or “buttons.” It is made from the crude lac in the same way as shellac, except that the fused shellac is run on to plates, where it solidifies into buttons about $\frac{1}{8}$ to $\frac{1}{4}$ inch in thickness. As a rule it is somewhat harder than ordinary orange shellac, owing to the small percentage of shellac wax that it contains.

Garnet Lac is similar to button lac, but contains more colouring matter. It is of a transparent ruby red colour when held up to the light.

Its value depends on the brightness and depth of its colour, for it is used for making coloured spirit varnishes. It is free from shellac wax, and dissolves in alcohol, giving a transparent deep red solution.

(2) THE HARD RESINS (FOSSIL GUMS)

AMBER

(Ambre Gris, Bernstein.)

Amber is probably the best known of all the resins or hard gums. It was familiar to the ancients under the names of electrum (from which the word electricity is derived) and succinum.

Amber is chiefly the fossil resin of a prehistoric conifer (*Pinus succinifer*) which grew on land now under the waters of the Baltic Sea. It is found in Denmark, France, and on the Essex and Suffolk coasts, but the main source of supply is the shores of the Baltic, where it is obtained either by dredging the sand along the seashore or else by mining.

The hardest of the fossil gums, amber was at one time extensively used in the manufacture of the best grades of varnish; but on account of its extreme scarcity and costliness it is now hardly ever used for this purpose.

Properties.—The colour of amber varies from a pale transparent yellow to a dark brown colour. It is graded, like most other fossil gums or resins, according to its colour and the size of the pieces.

Its specific gravity is about 1.07. When rubbed, as is well known, it acquires electrical properties.

On distillation it melts at about 350° C., and gives off water, succinic acid, and amber oil. It is practically insoluble in alcohol, ether, turpentine, and most other organic solvents.

ANIMI

(Animé.)

Animi is extensively imported into this country for use in the manufacture of the highest grades of varnish. After amber it is the hardest fossil gum known, and the varnishes made from it are noteworthy on account of their remarkable hard-wearing and durable properties.

Animi is imported from Zanzibar and from Dutch East Africa, and is the fossil resin remains of a tree known as *Trachylobium mossambicense*, which still flourishes in those regions.

The gum is found at a depth of about 2 ft. in the ground, and is dug up by native labour during the rainy season. The resin thus collected is washed free from the red sand with which it is contaminated, and is then sorted out into different grades according to its colour.

The best grades of animi have a pale yellowish colour, are semi-transparent, and are in the shape of long tears, the surface of which is covered with peculiar pock-marks known as "goose-skin."

The specific gravity of animi is about 1.068. When held in a flame it melts, then ignites, burning with a clear white flame, and giving off a pungent turpentine-like odour. The melting-point of animi is about 300° C.

It is not soluble in any of the ordinary organic solvents, and is unaffected by alkalis.

KAURI

(Kowree, Cowdee Gum, Cawree Gum.)

Kauri copal or gum kauri is a fossil or semi-fossil resin of various species of New Zealand pine trees (*Dammara Australis*).

The fossil resin is found mostly in the province of Auckland in open bush land, where but few trees now exist. The resin is obtained by digging, after which it is scraped to remove all earthy matter, and then graded according to colour and hardness.

Kauri comes on to the market in various grades, the best of which is known as "dial" kauri, the poorest as "bush" kauri.

Kauri gum is very highly esteemed, and is largely used in the manufacture of the best body and carriage varnishes.

More than two-thirds of the kauri gum shipped from New Zealand goes to the United States. In recent years it has become very scarce, and the price is almost prohibitive except for use in the manufacture of the highest grades of varnish.

The supplies appear to be getting gradually exhausted, and probably before many years it will be no longer in general use.

As a matter of interest it might be mentioned that some years before the war

the labourers engaged in the industry were almost entirely drawn from Austria-Hungary (principally Bohemia). Every year large numbers emigrated to New Zealand. In fact there was a regular traffic between the two countries, for so remunerative was the work that many of the emigrants were able in a very few years to return to their native land with considerable savings.

Properties.—Kauri gum has a conchoidal fracture and greasy lustre. The poorer grades have a peculiar brown woody appearance, which is quite characteristic.

Dial kauri is of a yellowish-white colour, powders with difficulty, and has a specific gravity of 1.079.

Bush kauri, which is collected at the foot of the tree, is of more recent origin than dial kauri, and is of a reddish-brown appearance and easily powdered.

Hard brown kauri gum melts at about 250° C.

Kauri gum is insoluble in turpentine and benzol, but partially soluble in alcohol and chloroform. On distillation it yields about 25 per cent. of kauri oil.

ANGOLA COPAL

Angola copal is a somewhat soft fossil gum, which is found in Angola, on the west coast of Africa. The best qualities reach the market in the form of large irregular lumps, known as white Angola copal, which is of a pale semi-transparent white appearance, and is used for making pale copal varnishes.

Its specific gravity is 1.062. It melts at about 210° C. Angola copal of a reddish colour is also put on the market, and is sold under the name of red Angola copal.

SIERRA LEONE COPAL¹

This fine resin is imported from Sierra Leone (West Africa). It is not fossil, but is produced by a leguminous tree called *Guibourtia copallifera*, and is collected in the same way as turpentine is in France. The pieces are irregularly spherical or elongated, usually small, and of a yellowish to a clear white colour. It is easily powdered. Its specific gravity is about 1.054. It melts at about 185° C.

It is used in the manufacture of the palest French oil varnishes.

PONTIANAC

This fossil gum is imported from Borneo, and comes on to the market in the form of large irregular-shaped lumps, varying in colour from a semi-transparent pale yellowish-white to a reddish-brown colour.

It is of a very hard glassy nature, and on being hit with a hammer splinters off into small pieces, which may be readily powdered.

Its specific gravity is about 1.062. It melts at about 280° C.

BENGUELA COPAL

This copal is obtained from equatorial Guinea, south of Angola, on the west coast of Africa. It is put on to the market in irregular lump form, and has a semi-transparent yellowish colour.

¹ A. Foelsing, "Chem. Rev. Fett-Harz-Ind.," xiv. 251.

It is a comparatively hard gum and is difficult to break; the fracture is of a brilliant glassy appearance. It melts at about 260°C .

CONGO COPAL

Congo resins are imported from the Belgian Congo. They are hard fossil gums, the colour of which varies from a semi-transparent pale whitish yellow to reddish brown.

It is very hard to fuse (its melting-point is 300°C .), and a considerable amount of volatile matter must be driven off before it will amalgamate with linseed oil. It breaks with a conchoidal fracture, with a shiny glassy lustre.

On account of the large supplies available, Congo gums are comparatively cheap, and are now being largely used in the manufacture of varnishes.

COLOURED RESINS

For the sake of completion it is perhaps desirable to give here a brief description of some of the more important of the very many naturally-occurring coloured resins and woody fibres, such as gamboge, dragon's blood, grass tree gum, red and yellow sanders wood, and others, which were formerly largely used for the purpose of colouring spirit varnishes.

These natural coloured resins have now been largely replaced owing to their lack of permanency by the synthetic coal tar dye-stuffs, and are now only used in special cases.

RED SANDERS WOOD

(Red Sandal Wood, *Pterocarpis Lignum*.)

Red sanders wood is the heart wood of *Pterocarpus santalinus*. It is imported in large heavy logs of a dark reddish-brown colour, the colouring matter of which is readily soluble in alcohol, but only sparingly soluble in water. For use in spirit varnishes the logs are cut up into chips, or, more often, rasped into a fine powder.

GAMBOGE

(Cambogia.)

Gamboge is a gum resin from *Garcinia Hanburii*, which grows in India, Ceylon and Siam. It is usually obtained as a yellowish-brown milky juice, which hardens in the air, by making incisions in the bark of the tree.

It is marketed in the form of lumps, cakes and sticks; is rather brittle and often covered with a yellow dust.

Gamboge contains about 80 per cent. of resin or gamboge yellow ($\text{C}_{30}\text{H}_{35}\text{O}_6$) which is readily soluble in ammonia, alcohol, or ether, giving a yellowish solution, which is distinctly acid.

It is used as a water colour by artists and also as a colouring matter in spirit varnishes and in making gold lacquer.

DRAGON'S BLOOD

This comes from various species of plants, but chiefly from the fruit of the *Calamus drago* of Sumatra, Indo-China and Molucca.

The brittle red resinous mass is obtained by shaking the ripe fruits into baskets and sifting out the impurities. The resin is then melted and moulded into sticks or cakes.

The best qualities have a deep blood-red colour. The specific gravity is about 1.25, and contains about 60 per cent. of a red resin. It has a peculiar acrid taste, and is readily soluble in alcohol, giving a blood-red solution.

It was formerly much used for colouring spirit varnishes, but is being gradually superseded for this purpose by the soluble spirit red aniline colours.

It melts at 100° C., emitting vapours of benzoic acid.

GUM ACCROIDES

(Acaroid Resins, Black-boy Gum, Grass-tree Gum.)

These resins are the product of various species of trees indigenous to Australia, such as *Xanthorrhoea Australis*.

There are two varieties, one the yellow gum accroides, and the other the red variety. Both varieties are soluble in alcohol. They are sometimes used for colouring spirit varnishes.

LAC

This natural-coloured resin has been described under Shellac.

CHAPTER XVI

DRYING OILS

DRYING oils is the name given to those oils which possess the property of forming a solid elastic substance when exposed to the air in thin films, *e.g.* linseed oil and wood oil. This drying property is due to these oils gradually absorbing oxygen from the air, and decreases as the iodine absorption value of the oil diminishes. When a drying oil is converted into a solid elastic film it is said to "dry."

A non-drying oil, such as olive oil and castor oil, on the other hand, will remain liquid at room temperature for an indefinite period.

Semi-drying oils, like cotton-seed oil and maize oil, lie between the two.

By far and away the most important of the drying oils is linseed oil, which is used in enormous quantities in the paint and varnish industries.

LINSEED OIL

Linseed oil is obtained from the seeds of the flax plant *Linum usitatissimum* which is grown in large quantities in the Argentine, India, United States, Canada and Russia.

The seeds are brown in colour, and contain 36 to 42 per cent. of oil, practically all of which may be extracted with the aid of suitable solvents.

Linseed is imported into this country chiefly from the Argentine (Plate oil) and India (Calcutta oil). The seed grown in Canada and the United States is used for home consumption.

Formerly large quantities of linseed were imported from Russia (Baltic oil), and owing to the purity of this seed the oil extracted therefrom was highly valued, being much superior as regards drying properties to either Plate or Calcutta oil.

As linseed oil is mainly used in the paint and varnish industries, the relative drying properties of the oil extracted from the different seeds imported is of the utmost importance. The variation in the drying properties of the different linseed oils is due mainly to the linseed containing other foreign seeds mixed with it, such as hemp, rape and mustard.

Composition.—To determine the relative proportions of the constituents in linseed oil is a problem which presents great difficulties. According to Fahrion¹ the average composition is approximately as follows :—

¹ Fahrion, *Zeitsch. Angew. Chem.*, 1910, 23, 1106.

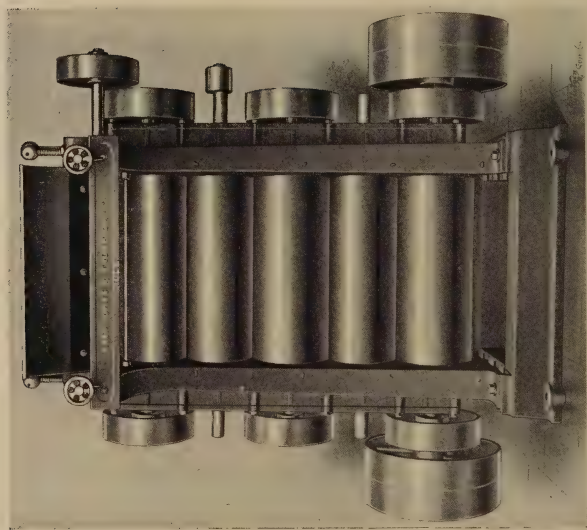


FIG. 24.—ANGLO-AMERICAN ROLLS.

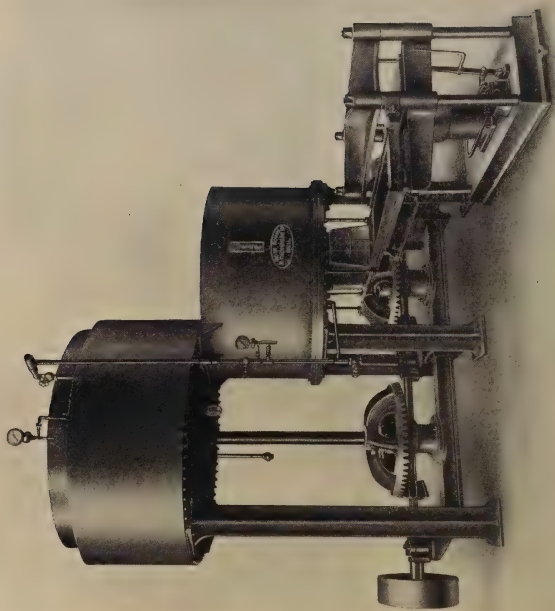


FIG. 25.—LINSEED HEATING KETTLES OR COOKERS WITH STEAM MOULDING MACHINE. (Rose, Dowds & Thompson, Ltd.)

Unsaponifiable matter.	0.6 per cent.
Saturated organic acids	9.3 "
Oleic acid	17.5 "
Linolic acid	30.0 "
Linolenic acid	38.0 "
Glyceryl radicle	4.6 "
	<hr/> 100.0 <hr/>

EXTRACTION OF LINSEED OIL

Linseed oil can be extracted from linseed either by means of solvents or else by pressure. The highest yield of oil is obtained when the extraction is carried out by the aid of solvents, but the resultant "cake"—which is a valuable by-product—is unsuitable for cattle feeding. Hence the method employed in practice is to extract the oil by pressure; when this is done about 10 per cent. of oil is left in the press cakes.

Extraction by Pressure

The early methods in vogue for expressing linseed oil were very crude, and simply consisted in packing the linseed in bags and squeezing out the oil by means of hand-presses.

At the present time the bulk of the linseed oil that comes on to the market is obtained by the Anglo-American system, in which powerful hydraulic presses are used, by means of which a pressure from 2 to 3 tons per square inch can be obtained.

The first stage in the Anglo-American process is the crushing of the linseed. The linseed is fed into a hopper, and passes through a series of four or five revolving chilled-steel rolls, whereby the seed is crushed into an extreme fine state of subdivision (Fig. 24). The crushed seed ("meal") is then conveyed to a cast-iron steam jacketted kettle (Fig. 25), where the seed is heated to about 180° F., and agitated by a revolving stirrer. Steam is blown into the mass in order to moisten it to the requisite degree.

The cooked linseed meal is next moulded into cakes of uniform size, conveyed to the Anglo-American press, where it is subjected to a pressure of about $1\frac{3}{4}$ tons to the square inch (Figs. 26 and 27).

The oil thus expressed is pumped into large storage tanks; it is as a rule turbid owing to the presence of albuminous and mucilaginous matters; but after standing about a week the impurities settle out, and the oil becomes perfectly clear and transparent, when it is ready for use. The "spawn" or mucilage which settles out on tanking contains phosphates of lime and magnesia.

The actual yield of oil obtained by this process is about 28–30 per cent.

Extraction by Solvents

This process gives the highest yield of oil, but the resulting "cake" is not suitable for cattle feeding, not only on account of its low oil content, but also because it is extremely difficult to remove completely all traces of the solvents used.

On this account this process is only used in those cases where the seed is in very bad condition due to bad storage conditions, either before or during shipment.

In this process the crushed seed is packed in perfectly air-tight vessels, through which the solvents flow. The solvent is continuously distilled off by steam, condensed, and returned to the extracting vessels till all the oil has been extracted, when the vessels are emptied and recharged with a fresh supply of crushed seed (Figs. 28 and 29).

The solvents in most general use are petroleum ether, carbon di-sulphide, carbon tetrachloride, and trichlor-ethylene.

Properties and Uses.—Cold-pressed oil is of a light-yellowish colour, with a characteristic pleasant odour and taste.

Warm-pressed oil is of a yellowish-brown colour, and the taste and odour are more pronounced and not quite so agreeable as in the case of the cold-pressed oil.

The specific gravity is about 0.930–0.931 at 15.5° C. (Baltic oil is 0.934).

Linseed oil differs from most other vegetable oils in remaining liquid at 0° C. and below. It thickens at about –19° C., and at about –29° C. solidifies to a solid yellow substance.

When heated it gives off pungent vapours containing moisture and acrylic acid. It flashes at 260° C.

Linseed oil is readily soluble in ether, turpentine, chloroform and similar solvents; but only partially soluble in alcohol.

Strong sulphuric acid rapidly chars linseed oil causing it to become thick and

of a black colour. Strong nitric acid converts it into a viscous, yellowish mass.

Linseed oil readily absorbs iodine and bromine owing to its high content of glycerides of unsaturated acids. The iodine value is one of the readiest means of determining the purity of a linseed oil.

When exposed to the air in a thin film, linseed oil gradually absorbs oxygen, ultimately yielding a solid elastic mass known as linoxyn.

This oxidation product is highly resistant, and is very insoluble in most oil solvents. It is on account of this property, and the brightness and elasticity of

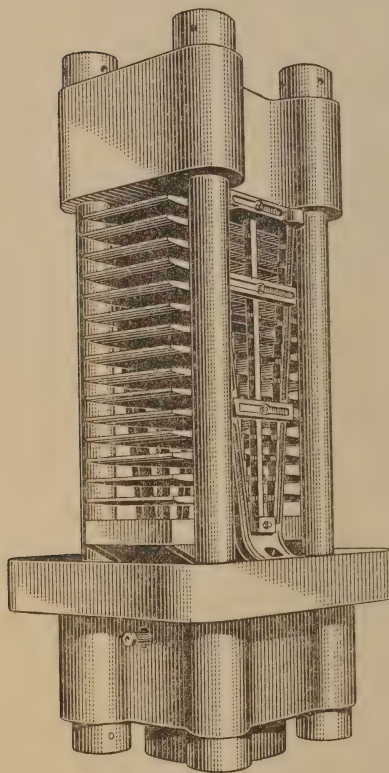


FIG. 26.—ANGLO-AMERICAN PRESS.

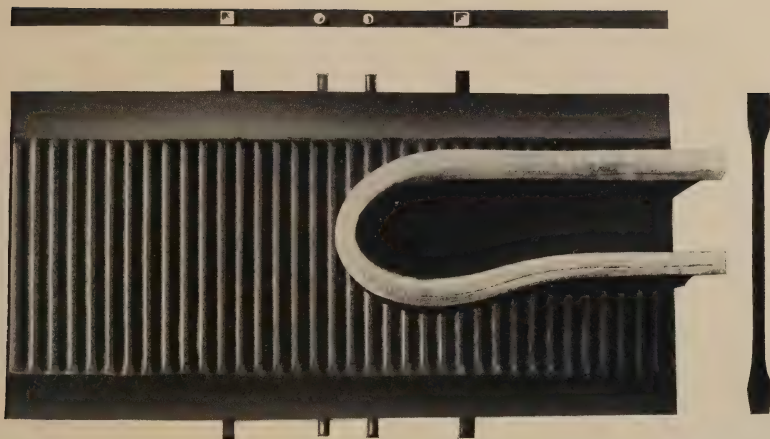


FIG. 27.—VIEW OF SOLID ROLLED STEEL PRESS PLATES, AS SUPPLIED WITH ANGLO-AMERICAN PRESS, SHOWING ELEVATION, LONGITUDINAL ELEVATION AND CROSS SECTION OF THE PLATES BENT COLD.

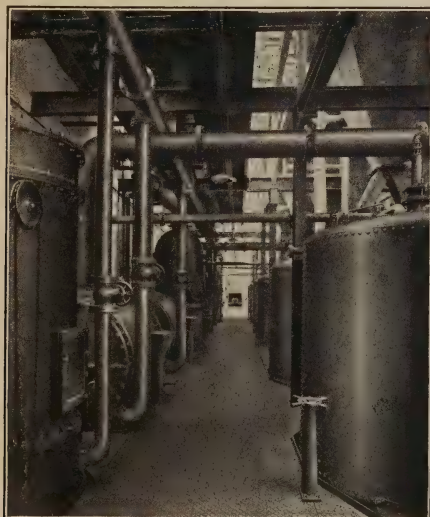


FIG. 28.—OIL EXTRACTION BY SOLVENTS—VIEW SHOWING EXTRACTION VESSELS, CONDENSER, EVAPORATORS, ETC., IN LARGE EXTRACTION PLANT. (Rose, Downs & Thompson, Ltd.)

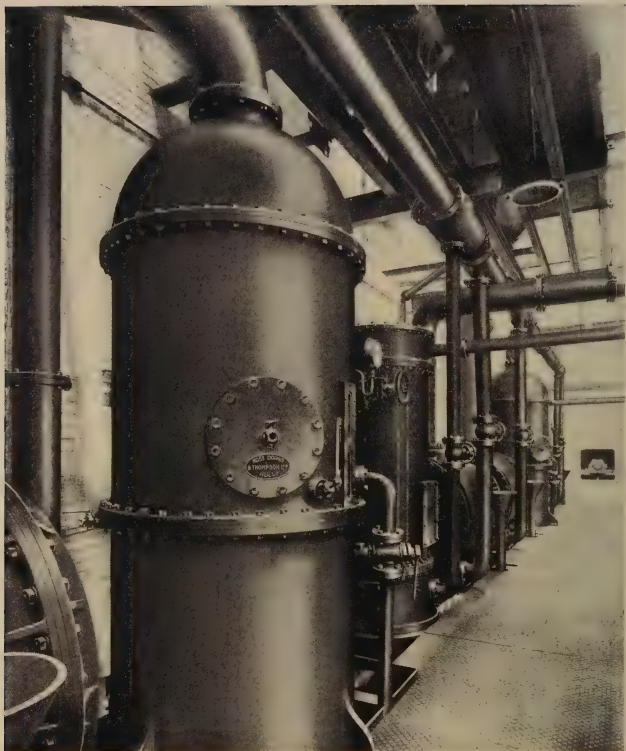


FIG. 29.—OIL EXTRACTION BY SOLVENTS—EVAPORATORS AND CONDENSERS
IN LARGE EXTRACTION PLANT. (Rose, Downs & Thompson, Ltd.)

the skin so formed, that linseed oil is so valuable as a vehicle for paints and varnishes, and in the manufacture of linoleum and waterproofing materials.

If thin glass or aluminium plates are coated with a thin film of linseed oil, weighed, and then placed in a dust-free atmosphere in a room of uniform temperature, and weighed at intervals of 12 hours, it will be found that there is a period of induction when no appreciable change of weight takes place. After this period a rapid increase of weight takes place, which rises to a maximum after about 100 hours, after which the oil very slowly loses in weight.

The increases in weight show considerable variation, namely, from 14 to 26 per cent., the average amount being 18 per cent. The value thus obtained is known as the "Oxygen figure."

It has been shown that while this increase of weight is going on—due to the absorption of oxygen—decomposition is taking place and gaseous products are being evolved.

The chemical composition of the vapours evolved from linseed oil during drying have been fairly accurately determined. It has been shown that water constitutes the bulk of these products, together with traces of carbon dioxide, formic acid, acetic acid, acrylic acid, butyric aldehydes, and a minute trace of carbon monoxide.¹

Linseed oil, besides being extensively used in the paint, varnish, and linoleum trades, is also used in the manufacture of soap and putty.

Linseed oil is extensively "hardened" by hydrogenation, with a nickel catalyst, producing a very fine hard stearine, which is largely used in the soap and margarine industries.

Average Analytical Constants for Linseed Oil

Specific gravity at 15.5° C.	0.930-0.934
Acid value	6.0
Saponification value	190
Iodine value (Wijs)	180-185
Refractive index 40 C° (Z B)	73
Unsaponifiable matter	0.5-1.5 per cent.
Solidifying point of fatty acids	19.5° C.

SCHEME FOR THE ANALYSIS OF LINSEED OIL

Raw linseed oil obtained from the oil mills may be taken to be commercially pure. It is rarely if ever found to be adulterated, in spite of the formidable list of adulterants such as rosin oil, mineral oil, fish oil, and many others enumerated in the various text books dealing with the subject.

Without recourse to tedious methods of analysis, the taste and smell of the oil alone should be quite sufficient to indicate the presence of these adulterants if existent in more than minute quantities.

An adulteration with 10-20 per cent. of soya bean oil would be more difficult to detect, but in this case the retardation of the drying properties, accompanied by the decreased iodine value, would readily reveal its presence.

¹ C. A. Klein, *Chem. World*, 1914, 3, 250. Gardner, *J. Ind. Eng. Chem.*, 1914, 6, 91.

Hemp seed oil might also be used, but its value as a rule approximates to that of linseed oil.

When it is desired to test the purity of linseed oil, and its suitability for use in the manufacture of paints and varnishes, the following tests should be carried out (*Note*.—This scheme of analysis is also applicable to all animal and vegetable oils):—

(1) SPECIFIC GRAVITY

Take a 50 c.c. gravity bottle (Fig. 21), and weigh it accurately to four decimal places. Fill with distilled water, and place in a water bath maintained at 15.5° C. for 15 minutes. Insert the stopper and remove the water that oozes from the top. Dry quickly with a clean dry cloth, holding the bottle by the neck, and weigh. Repeat this operation so as to make quite sure the result is correct. By this means the volume of the bottle is accurately determined once for all and the necessary \pm correction factor found.

The bottle is next emptied and carefully dried in the steam oven. Linseed oil is next introduced, and the method of cooling, drying, and weighing carried out precisely in the same manner as in the case of the water.

As the specific gravity is the weight of any volume of a substance compared with the weight of an equal volume of pure water at a standard temperature (15.5° C.), all that is necessary is to divide the weight of the oil obtained by that of the weight of an equal volume of water.

Example.

Weight of 50 c.c. gravity bottle	25.5301	gms.
„ „ „ + water at 15.5° C.	75.4503	„
„ water at 15.5° C.	49.9202	„
„ bottle + linseed oil at 15.5° C.	72.0602	„
„ bottle	25.5301	„
„ oil at 15.5° C.	46.5301	„

$$\frac{\text{Weight of linseed oil at 15.5° C.}}{\text{Weight of water at 15.5° C.}} = \frac{46.5301}{49.9202} = .9322 \text{ specific gravity of linseed oil;}$$

or shortly, as correction = .080 weight of linseed oil = $46.5301 + .080 = 46.6101 \times 2 = 93.2202 \therefore$ specific gravity of linseed oil = .9322.

The specific gravity may also be obtained by weighing the oil in a Sprengel tube, by the Westphal balance, or by means of hydrometers.

(2) ACID VALUE OR FREE ACIDITY

Free acidity equals the percentage of oleic acid present in an oil.

$$1 \text{ c.c. } \frac{N}{1} \text{ KOH} = 0.282 \text{ gms. oleic acid.}$$

Acid value equals the number of milligrams of potassium hydrate required to neutralise the free fatty acids in 1 gm. of oil.

Determination of Free Acidity

$\frac{N}{5}$ KOH or Na OH (aqueous solutions) are the best.

Weigh out about 15 gms. (quantity optional). Dissolve in 50–66 c.c. neutral alcohol, and titrate with $\frac{N}{5}$ KOH solution, using phenol phthalein as indicator.

Although linseed oil is only partially soluble in alcohol, the free fatty acids are generally very much more soluble.

If preferred the oil may be dissolved in methylated ether, and the neutral alcohol then added.

If mineral acids be present these can be neutralised by the potash, using methyl orange as indicator; and when the solution has turned from red to yellow the titration can be continued with phenol phthalein as the indicator.

(3) SAPONIFICATION VALUE

The saponification value is the number of milligrams of potash required to saponify one gram of oil. The number of grams of oil saponified by one equivalent of potash, *i.e.* 56.1 grams of potash, is termed the saponification equivalent.

Free fatty acids in an oil raises its saponification value; whilst on the other hand any considerable quantity of unsaponifiable matter proportionately reduces this figure. The determination of the saponification value of linseed oil is carried out as follows:—

Solutions $\frac{N}{2}$ HCl (*i.e.* 1.325 Na₂CO₃ to 50 c.c. HCl solution).

„ $\frac{N}{2}$ approx. potash hydrate in redistilled alcohol; made by dissolving

35 grams of potash hydrate (pure by alcohol) in 1 litre of alcohol.

Weigh out under 4 grams of the oil, run in 30 c.c. alcoholic potash solution. Boil, with frequent shakings, under a reflux (a long, wide glass tube) till the solution is quite clear.

If mineral oil be present, it will remain undissolved, or separate out on cooling the flask.

Titrate the excess potash by $\frac{N}{2}$ HCl solution. Do a blank under the same conditions. It is not necessary, unless preferred, to add any water before titration.

Number of c.c. $\frac{N}{2}$ HCl for blank minus number of c.c. $\frac{N}{2}$ HCl used in titrating excess of potash \times by 28 divided by weight of oil taken equals saponification value.

(4) UNSAPONIFIABLE MATTER

Weigh out 5 grams of the oil into a 6-inch porcelain basin. Add 25 c.c. of 2 N alcoholic NaOH solution, and evaporate the alcohol gently, with occasional stirring, to dryness.

Add a further 25 c.c. of alcohol and 2.5 gms. pure soda bicarbonate (NaHCO_3) and again evaporate to dryness. Just before this point is reached stir well in 50 gms. ignited sand, and place in water oven for one hour till no smell of alcohol is perceived.

Extract in a soxhlet (see Fig. 7) with methylated ether till all the unsaponifiable matter is taken out. Wash this extract with warm water to wash out any dissolved soap. Generally three washings are sufficient. Always have a large bulk of ether present to lessen the error due to the washing. Then distil off the ether in a tared vessel and weigh.

Examination of the Unsaponifiable

In pure linseed oil the unsaponifiable rarely exceeds 1 per cent. This also applies to most oils with the exception of rosin oil, marine animal oils, such as sperm, porpoise, shark-liver, and a few other oils.

If the unsaponifiable be alcohols, they are soluble in cold ethyl alcohol. This is not the case with most mineral oils.

Alcohols and cholesterols, etc., are soluble in boiling acetic anhydride (do this under a reflux, boiling for two hours).

Rosin oil gives the characteristic test with the Lieberman-Storch reaction (acetic anhydride + 1.53 sulphuric acid); also, rosin oil will dry.

If soap is thought to be present in the unsaponifiable it may be ashed, when sodium oxide Na_2O is left—otherwise there should be no ash.

(5) IODINE VALUE

The iodine value of linseed oil is of the utmost importance in determining its purity.

Hübl in 1884 found that by dissolving an oil in a suitable solvent, such as chloroform or carbon tetrachloride, and adding a solution of iodine and mercuric chloride in 95 per cent. alcohol, iodine is absorbed fairly rapidly during the first two hours, and more slowly afterwards. In about twenty hours absorption is complete. By taking a known quantity of iodine, and estimating with thiosulphate the excess remaining behind when the reaction is complete, the amount absorbed by 100 gms. of oil may be readily determined. This is known as the iodine value.

The iodine value depends on the proportion of unsaturated fatty acids present; the higher the iodine value, as a rule, the greater the drying properties of the oil.

Perfectly pure saturated acids and glycerides have no iodine value.

It is generally assumed that a chloro-iodo addition compound is formed, one atom each of chlorine and iodine attaching themselves to the carbon atoms at each double bond, thereby yielding saturated derivatives.

Hübl's process for the determination of the iodine value, owing to the long period required for the complete absorption of the iodine, has now been replaced by modifications such as those of Wijs and Hanus whereby the action is complete in from two to three hours.

The Wijs modification is the one in general use in this country and is carried out as follows :—

Solutions

ICl Solution.—Dissolve 7.2 gms. of iodine and 7.35 gms. of iodine trichloride in a litre of pure glacial acetic acid.

Ki Solution.—Dissolve 10 gms. of potassium iodide in 100 c.c. distilled water.

Thiosulphate Solution.—Dissolve 23.5 gms. of pure sodium hyposulphite in a litre of water, of such a strength that 30 c.c. ICl solution requires 50 c.c. $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Weigh out 0.15 gms. (7 drops) of the oil into a clean dry 12-oz. bottle, provided with a ground glass stopper.

To weigh out the oil accurately, cut off a small piece of tube $\frac{1}{4}$ inch long, seal one end, and flatten out while hot so that it will stand upright, and use this as the oil container. Introduce the right amount of oil and accurately weigh; then slide gently into the 12-oz. bottle.

Now add 10 c.c. pure carbon tetrachloride and run in 30.1 c.c. ICl solution (and count as 30 c.c.), shake gently, and place in a dark cupboard for one hour.

Do a blank under the same conditions.

Then add 10 c.c. by pipette 10 per cent. KI solution and 100 c.c. water. Shake well, and titrate the excess iodine by the $\text{Na}_2\text{S}_2\text{O}_3$ solution, using starch as indicator.

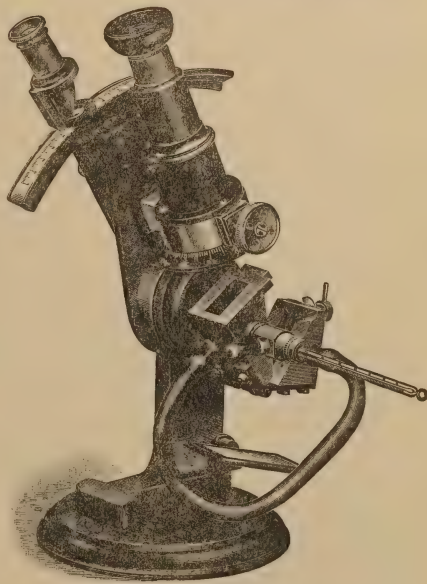


FIG. 30.—REFRACTOMETER.

Hanus Method

This method is largely used in America, and is carried out as follows :—

Dissolve 13.2 gms. of iodine in 1000 c.c. of pure glacial acetic acid. Add enough bromine to double the halogen content, determined by titration—3 c.c. of bromine is about the proper amount. Proceed as described under the Wijs process.

In both processes it is necessary that a large excess (50 per cent.) of iodine should be present.

Wijs solution may also be made by dissolving iodine in pure glacial acetic acid and passing in dry chlorine till the iodine is converted into iodine monochloride (ICl).

(6) REFRACTIVE INDEX

The refractive index is of great value in determining the purity of linseed oil, and is preferred by some chemists even to the iodine value.

It is determined by using a properly standardised refractometer such as the Pulfrich, Abbe or Butro-Refractometer (Fig. 30).

Qualitative Tests on Raw Linseed Oil

Rosin.—Rosin, or rosin oil, may be readily detected if present by the Liebermann-Storch test, which is carried out as follows:—Gently warm a small portion of the linseed oil with an equal volume of pure acetic anhydride; cool; pipette off the acetic anhydride layer, and add to it one drop of sulphuric acid S.G. 1.53 (by mixing 34.7 c.c. conc. sulphuric acid with 35.7 c.c. of water). In the presence of rosin a fugitive violet coloration is produced.

The amount of rosin present may be estimated, if required, by the Twitchell method. In this process the sample of oil is saponified, and then treated with mineral acids whereby the fatty acids and rosin acids are liberated.

The dried mixed fatty and rosin acids are weighed accurately, and dissolved in ten times their volume of absolute alcohol, and saturated with dry HCl gas. The fatty acids are converted into esters, while the rosin acids are unaffected.

The esters and rosin acids are washed free from acid, dissolved in alcohol, and titrated with N alkali, using phenol phthalein as indicator.

Number of c.c. of alkali required $\times 0.346$ = rosin acids present.

Mineral Oil.—Take a large boiling tube half full of alcohol (90 per cent.) and add a piece of caustic potash (pure by alcohol) about the size of a pea and warm till dissolved. Add 3 drops of linseed oil and boil for three minutes, allowing the alcohol to rise well up to the sides of the tube. Fill up with distilled water.

The solution will be perfectly clear unless mineral oil is present, when a milky white solution is obtained.

Cotton-seed Oil.—This is detected by the Halphen colour test, which is carried out as follows:—

Make 1 per cent. solution of flowers of sulphur in carbon bisulphide and add it to an equal volume of the oil dissolved in its own volume of amyl alcohol.

Stand in boiling water for about ten minutes, when a deep red coloration is produced if any cotton-seed oil is present.

Fish Oils.—Add 2 drops of conc. sulphuric acid to the oil. If fish oils be present a purple brown coloration is produced.

Specification for Raw Linseed Oil

(1) The oil must be of clear transparent pale yellowish colour, and have a pleasant odour and taste. It must not be turbid or contain any foots.

- (2) The oil must be genuine and free from admixture with mineral or other oils.
- (3) Three drops spread out evenly on a piece of ground glass 4 in. by 3 in., and placed in a water oven at 100° C. must dry to a hard film in sixty minutes.
- (4) The specific gravity of the oil at 15·5° C. must not be less than 0·930 nor greater than 0·936.
- (5) The refractive index of the oil at 40° C. (Z B) should be not less than 72 nor greater than 74.
- (6) The acid value of the oil must not be greater than 4.
- (7) The saponification value of the oil must not be less than 187 nor greater than 195.
- (8) The oil should contain not more than 1·5 per cent. of unsaponifiable matter.
- (9) The iodine value of the oil (determined by the Wijs method) should not be less than 175.
- (10) On ignition the oil should not yield more than 0·25 per cent. of ash.

REFINED LINSEED OIL

Raw linseed oil which comes from the press is always turbid and is tanked so as to clear itself and get rid of water and mucilaginous impurities, which settle to the bottom of the tank as foots.

The colour of this oil is too deep for many purposes, and hence it is subjected to a refining process so as to bleach out a lot of the colouring matter present.

For artists' oil it is usual to expose the raw oil in shallow tanks covered with glass to the sunlight over a period of three or four months, whereby the chlorophyll and allied compounds, which cause the deep colour of the crude oil, are bleached out, leaving an oil of a very pale colour.

For ordinary commercial purposes, however, it is usual to refine it in the following manner:—5 to 10 tons of oil are pumped into a large tank fitted with blowers so as to agitate the oil thoroughly. About 1½ to 2 per cent. of fairly conc. sulphuric acid is then added to the oil, which is well agitated; the mucilaginous matter is thereby partially charred, and as it sinks to the bottom it carries other suspended impurities with it. Water is next run in, and the whole mass well agitated by blowing in air, and then allowed to settle for twelve hours. The black oily mass that separates out at the bottom is known as “black strap oil” and is run off with the water.

The oil is again well washed with hot water to remove any traces of acid that may be present, allowed to settle, and drawn off into tanks ready for use.

Refined oil is used in all those cases where the colour of the ordinary raw linseed oil would be objectionable, such as in the grinding of white lead and other white pigments.

BOILED OIL OR BOILED LINSEED OIL

The reason why linseed oil is so valuable a medium in the paint and linoleum trades is on account of its drying properties, due to its high content of glycerides of unsaturated acids.

Linseed oil when spread in thin films absorbs oxygen from the air and is converted into "linoxyn," a tough elastic body which is very insoluble and not readily acted on by chemical agents, and has a composition represented by the formula $C_{57}H_{92}O_{24}$.

This property of absorbing oxygen is greatly increased by heating the oil to about 300° F. or higher in the presence of certain metallic oxides, such as the oxides of lead, manganese and cobalt.

These oxides are known as siccatives or dryers (see Chapter XX.), and if they are suitably chosen and used in the right proportions, and at suitable temperatures, enable the linseed oil to dry to a hard film in about eight hours instead of two or three days, which is the normal time. This is of the utmost importance in the paint, varnish and linoleum trades.

Linseed oil which has been heated with dryers is known as boiled oil.

The metallic oxides act as oxygen carriers or catalysers, accelerating the speed at which the oil absorbs oxygen from the air, and thus the formation of "linoxyn."

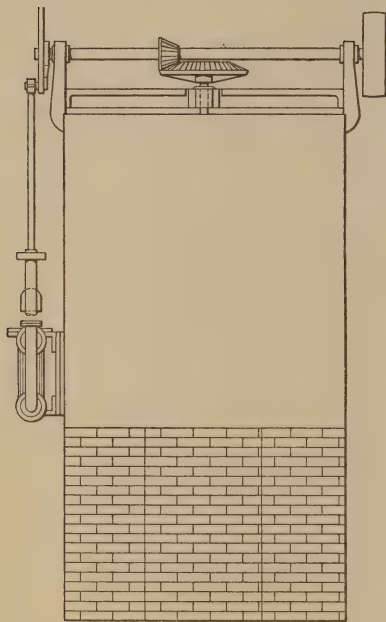


FIG. 31.—LINSEED OIL BOILING PAN,
HEATED BY STEAM.

BOILING LINSEED OIL

The oil according to the old-fashioned method was heated by direct fire heat in iron or copper pans to about 300–400° F., and the driers, consisting of litharge, red lead, and manganese dioxide, stirred in till completely taken up.

By this means a heavy-bodied dark boiled oil was produced, which dried in about eight hours with a tough hard film.

Fire-boiled oil is still preferred in some trades, such as, for example, in the manufacture of waterproof sheetings, on account of its hard drying qualities.

In a modern oil-boiling plant the usual process consists in heating from 5 to 10 tons of oil at a time in large iron pans, provided with stirrers and blowers, and heated with superheated steam (Fig. 31).

The oil is pumped into the pan until it is three-quarters full, and is heated with steam, whereby the temperature of the oil is gradually raised. At about 220° F. a considerable amount of frothing takes place, due to the evolution of moisture in the form of steam.

At about 300° F. the stirrers are set going and the requisite amount of driers added.

The driers in general use are mixtures of lead and manganese resinates or linoleates, but the resinates or linoleates of cobalt may also be used.

The oil is now blown, and the temperature is maintained at about 300° F. for eight hours. Samples are drawn off from time to time. When the required colour is obtained, then the stirrers are stopped and the steam and blowers shut off, and the whole left for twelve hours to settle out.

During the process of boiling the oil undergoes some decomposition. Water is continually being given off, accompanied by large quantities of acrolein C_2H_3CHO , a derivative of glycerine, which is recognised by its penetrating acrid odour and by its powerful action on the lachrymal glands of the eye.

The quantity of driers used depends on the kind of oil that is required—that is, whether pale or dark. Care should be taken not to use excessive quantities of driers, as these would accelerate the rate of drying to such an extent that the films produced from such oils would be crinkly and spotty.

The function of the manganese, lead and cobalt driers in boiling oil is to take up oxygen from the air and transfer it to the oil; and in so doing they undergo alternately the process of oxidation and reduction.

Properties and Uses of Boiled Oil

Boiled oil varies in colour from a pale straw yellow (bleached boiled oil) to a dark reddish colour (double boiled oil), according to the nature and amount of driers used and the temperature at which the oil has been boiled.

The specific gravity varies from 0.940 to 0.950, and the time of drying from eight to twenty-six hours.

The following grades of boiled oil come on to the market:—Double boiled oil, single boiled oil (*i.e.* ordinary boiled oil), pale boiled oil, bleached pale boiled oil.

On account of its rapid drying property boiled oil is largely used as a paint and varnish medium, and also in the linoleum trades.

Specification for Boiled Oil

1. The boiled oil must be pure old tanked boiled linseed oil, transparent, and equal in depth of colour to the standard. It must not contain foots or other suspended matter.

2. The oil should be free from admixture with mineral oils or any other oils, and contain not more than 2 per cent. of rosin or resinates.

3. The specific gravity at 15.5° C. must not be less than 0.940 nor greater than 0.950.

4. A thin film of the oil when spread out on glass should dry at ordinary room temperature in not more than twenty-four hours.

5. The acid value of the oil should not be greater than 6.

6. The iodine value of the oil (Wijs method) should be not less than 170.

7. The oil should not contain more than 2 per cent. unsaponifiable matter, and on ignition should not give more than 1·5 per cent. of ash.

Scheme for the Analysis of Boiled Oils

The analysis of a boiled oil should be carried out according to the scheme given for the analysis of raw linseed oil.

Boiled oils are much more liable to be adulterated than raw oils, the usual adulterants being a small amount (1·2 per cent.) mineral oil, rosin oil, or more usually an excessive amount of rosin in the driers; also soya bean oil, menhaden oil, and any other drying oil that should happen to be cheaper than linseed oil at the time when the oil is boiled.

Bung Boiled or Bung-hole Boiled Oils.—This is the name given to linseed oil to which about 10 per cent. of terebine has been added to make it dry somewhat like boiled oil. These oils generally contain a lot of foots, and their drying properties are very unsatisfactory.

Raw and Boiled Oil Substitutes.—When linseed oil is high in price large amounts of raw and boiled oil substitutes are put on the market, and extraordinary claims are made as to their value.

As a rule these substitutes are of very little value, and cannot be regarded in any way as being equal to linseed oil or capable of replacing it except in the case of the cheapest class of export paints.

These substitutes are usually made from common rosin which has been treated so as to render it non-feeding, and thinned down with an equal weight of petroleum thinners. In addition they sometimes contain about 10 per cent. of fish oil to help to soften the rosin and make it less brittle.

The better class of linseed oil substitutes are frequently made by thickening linseed oil or fish oils (or a mixture of both) by blowing with air, or by treatment with sulphur, till a very thick-bodied oil is produced. This is then thinned down to the right consistency with petroleum thinners. In the case of the boiled oil substitutes—as will be understood—it is necessary to add a comparatively large quantity of lead and manganese driers in order to get the desired drying properties.

The following analyses by the author of “Raw and Boiled Oil Substitutes” will give an indication of their composition:—

1		2
<i>Raw Oil Substitute.</i>		<i>Boiled Oil Substitute.</i>
Specific gravity at 15·5° C.	0·930	0·932
Acidity (oleic acid)	26 per cent.	22 per cent.
Unsaponifiable on the residue	12·20 „	12·89 „
Loss on heating (white spirit)	46·6 „	43·0 „
Residue (rosin+approx. 10 per cent. mineral oil)	53·4 „	57·0 „

The raw oil substitute contained a trace of lead, whilst the boiled oil substitute contained about 2·5 per cent. of lead and about ·5 per cent. of manganese (Mn).

3

Boiled Oil Substitute

Specific gravity at 15·5° C.938
Acidity (as oleic acid)	. . .	3·5 per cent.
Loss on heating (white spirit)	. . .	48·50 „
Residue	. . .	51·50 „

The residue consisted of a thickened oil, with a very small amount of rosin, and contained lead and manganese driers.

CHINESE WOOD OIL (TUNG OIL)

Tung oil is obtained from the seeds of *Aleurites cordata*, which grows in China, Japan and Cochin China. Large quantities of this oil are now exported from China to this country and America for use in the paint and varnish industries.

The best grades of wood oil are shipped from Hankow and are sold as Hankow wood oil.

The Japanese wood oil is not considered to be equal to the Chinese.

Extraction of the Oil

The methods in vogue are still very primitive. The cold pressed oil, which is the quality mainly exported, is obtained by the natives by crushing the seeds and extracting the oil by means of hand presses.

Sometimes the seeds are roasted over fires and ground between stones before expression; when this procedure is adopted a greater yield is obtained.

The seeds contain about 50 per cent. of oil. The oil cake is poisonous, and hence can only be used as a fertiliser.

The crude oil is allowed to settle and is then filtered through coarse sacks and sold to the Chinese merchants, who export it to Europe, no chemical refining being necessary.

Chemical Composition

Wood oil contains a large proportion of the glyceride of oleomargaric acid (oleostearic acid $C_{17}H_{31}COOH$), a stereo-isomeride of linolic acid.

Properties and Uses

The colour of wood oil varies from a pale yellow to a dark brown, the paler oils being more highly esteemed. It has a distinctive odour.

In its natural state wood oil dries rapidly with a flat, waxy, white surface, which has a frosted appearance. It is used by the Chinese as a natural wood varnish for coating the bottoms of their junks to render them waterproof. It is also largely used in this country on account of its water-resisting properties in the manufacture of boat and yacht varnishes.

At about 0° C. the oil solidifies to a white waxy mass. On heating the oil to

293° C. (560° F.) for about ten minutes it polymerises, and is converted into a stiff jelly, which can be cut with a knife.

Iodine dissolved in chloroform and added to 20 per cent. solution of the oil in chloroform causes it to solidify rapidly.

Wood oil is largely used in conjunction with rosin in the preparation of wood oil varnishes (see Chapter XVIII.).

Wood oil fatty acids in combination with lead, cobalt, etc., make excellent driers (lead tungate, etc.).

Average Analytical Constants for Wood Oil

Specific gravity at 15.5° C.	=	0.941
Saponification value	=	191
Acid value	=	4
Unsaponifiable matter	=	0.5 per cent.
Iodine value (Wijs)	=	165
Refractive index 40° C. (ZB)	=	1.475

Scheme for Analysis of Wood Oils

The various analytical constants for wood oil are obtained according to the methods given under the scheme for analysis of linseed oil.

A very quick yet satisfactory method for determining the purity of a sample of wood oil is the heating or polymerisation test. This may be carried out in the following manner:—

Heat Test.—Place 100 gms. of the oil in an open metal pan 6 inches in diameter and heat rapidly to a temperature of 540° F. Keep the oil at about this temperature and stir well till it begins to solidify. Note the time required after the oil reaches 540° F. till it begins to solidify. This should not exceed 7½ minutes for any good quality of wood oil.

When the oil has solidified in the pan turn it out while still hot, and cut with a knife. Pure Hankow wood oil gives a pale, firm product, and cuts under the knife like dry bread without sticking.

If the oil requires longer than 7½ minutes to solidify after reaching 540° F., and the resultant product is dark, soft or sticky, then the oil is adulterated.

An alternate method consists in filling a large boiling tube nearly three-quarters full with the sample, and placing it in an oil bath heated to 293° C. (560° F.) along with a similar sized tube containing an equal volume of pure Hankow wood oil.

The oil bath is maintained at 293° C. for ten minutes. The tubes are then removed and the consistency of the jelly-like mass noted.

A pure oil should give a hard jelly which can be cut quite easily. If the oil contains 10 per cent. of, say, soya bean oil or linseed oil the jelly form will be quite soft and sticky.

Specification for Wood Oil

1. It should be pure Hankow wood oil, pale in colour, bright, and perfectly free from any admixture of other oils.

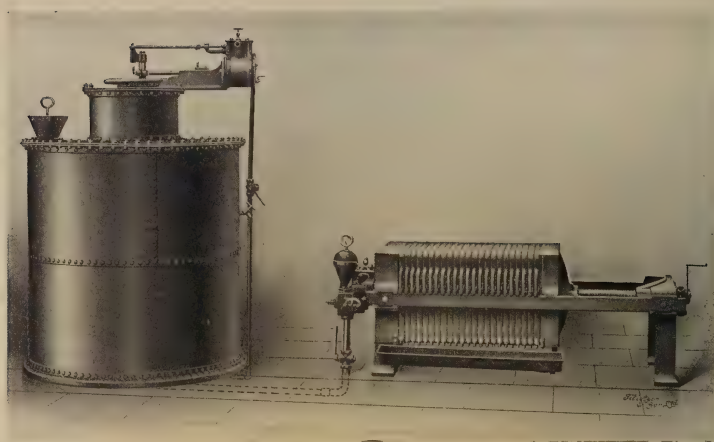


FIG. 32.—FULLER'S EARTH OIL REFINING PLANT. (Rose, Downs & Thompson, Ltd.)

2. The specific gravity of the oil at 15.5° C. should be between 941 and 942.
3. The refractive index of the oil at 40° C. should be about 1.475.
4. The oil should contain not more than 0.75 per cent. of unsaponifiable matter.
5. On heating a portion of the oil at 540° F. for ten minutes the resultant jelly-like mass should be hard and cut cleanly with a knife.
6. The saponification value of the oil must be not less than 190 nor greater than 195.
7. The iodine value (Wijs method) of the oil should be not less than 160.

SOYA BEAN OIL

Soya bean oil has been used as a substitute for linseed oil when the price of the latter, owing to short supply, has risen considerably above that of bean oil.

The soya bean (*Glycine hispida*) is native to China, Manchuria and Japan. The seeds, which are of the shape and size of a pea, contain about 18 per cent. of oil.

In recent years enormous quantities of the beans have been shipped from Manchuria to this country, chiefly to Hull, where the oil is extracted in the Anglo-American presses, a yield of about 10 per cent. of oil being obtained.

The cake after expression forms a valuable cattle food.

Soya oil is also obtained by extraction with solvents, a greater yield being thus obtained.

Properties and Uses

Soya bean oil is of a brownish yellow colour, but on refining by sulphuric acid, caustic soda, or Fuller's earth, a pale yellowish oil is obtained.

The plant (see Fig. 32) for refining soya bean oil (and other oils) with Fuller's earth consists essentially of (a) a vortex mixing kettle for mixing the Fuller's earth with the oil to be treated and (b) a filter press for subsequently removing from the oil the Fuller's earth together with all suspended matter, leaving the oil quite clean and bright.

Soya bean oil has a characteristic sweet odour and taste. It is largely used as an edible oil, and for the manufacture of soap.

As a paint oil it is not very satisfactory alone on account of its poor drying properties (iodine value 130); hence it is usually used in conjunction with linseed oil.

The manufacture of boiled soya bean oil from raw bean oil is carried out much in the same way as described under boiled linseed oil, but in this case a very much larger proportion of driers is necessary in order to produce a satisfactory drying oil. As a rule cobalt driers are used as giving more rapid drying properties to the bean oil.

Analysis.—See under Linseed oil.

Average Analytical Constants for Soya Bean Oil

Specific gravity at 15·5° C.	. . .	= 0·925
Acid value	. . .	= 0·5
Saponification value	. . .	=193
Iodine value (Wijs)	. . .	=130
Refractive index 40° C. (ZB)	. . .	= 63
Unsataponifiable	. . .	= 0·5 per cent.

PERILLA OIL

This oil owing to its superior drying properties and the hardness of the resulting film is finding an increasing use in the manufacture of paints and varnishes. The quantity available, however, is not very great, and its comparatively high price prevents its more general use.

It is obtained by expression from the nuts of the *Perilla ocimoides*, which is indigenous to China, Japan and the East Indies. It resembles linseed oil both in colour and smell. It is remarkable for its very high iodine value, which is the greatest of all known vegetable oils.

Average Analytical Constants for Perilla Oil

Specific gravity at 15·5° C.	. . .	= 0·935
Acid value	. . .	= 4·3
Iodine value (Wijs)	. . .	=205
Saponification value	. . .	=193
Refractive index at 40° C.	. . .	= 1·478

MENHADEN OIL (FISH OIL)

The fish oil most commonly used in the paint industry (especially in America) is the variety obtained from the body of the American fish *Alosa menhaden*, and is usually called menhaden oil.

The oil is obtained by boiling the fish in water or by a process of steaming. On settling, the oil rises to the surface, and is skimmed off. The residual fish remains are pressed to extract the remainder of the oil, after which they are dried and sold as fertilisers.

The oil thus obtained is rather brown in colour, and contains a lot of stearine; it requires to be bleached and filtered before use. The bleaching process tends to remove the objectionable smell of the oil.

Menhaden oil when boiled with driers yields a boiled oil which dries well, giving tough elastic films, which possess excellent waterproofing qualities. Its strong fishy smell prevents its more extended use in the paint industries, although in the linoleum trade a considerable quantity is used.

Average Analytical Constants for Menhaden Oil

Specific gravity at 15·5° C.	= 0·931
Saponification value	=192
Acid value	= 5
Iodine value	=165
Refractive index 40° C. (Z B)	= 72
Unsaponifiable	= 1 per cent.

It will be noted that the above figures show a remarkable similarity to those given by linseed oil.

HEMP SEED OIL

This oil is obtained from hemp seed (*Cannabis sativa*) which is cultivated in N. America, India and Japan. It has a greenish colour, which darkens with age, becoming brown. Occasionally it is used as a substitute for linseed oil, or as an addition to linseed oil when the difference in price makes it worth while.

It is not equal to linseed oil in drying properties, and on account of its colour can only be used in making dark coloured varnishes.

Average Analytical Constants for Hemp Seed Oil

Specific gravity 15·5° C.	= 0·928
Saponification value	=190
Acid value	= 0·75
Unsaponifiable	= 0·5
Iodine value (Wijs)	=175

WALNUT OIL

This oil is obtained from the common walnut (*Juglans regia*), which contains over 60 per cent. of oil. Cold-pressed oil is commonly produced, which is almost colourless and has an agreeable taste, and an odour of walnuts. Hot-pressed oil is greenish in colour, with an acrid flavour.

Cold-pressed oil bleaches quickly in sunlight, and because of its pale colour is used as an artists' oil, and in the preparation of fine varnishes.

Average Analytical Constants for Walnut Oil

Specific gravity at 15·5° C.	= 0·926
Saponification value	=193
Acid value	= 1·75
Unsaponifiable	= 0·5 per cent.
Iodine value (Wijs)	=150
Refractive index 40° C. (Z B)	= 65

POPPY SEED OIL

This oil is made by pressing the seeds of the poppy (*Papaver somniferum*), which grows in India, Russia and France. The seeds contain 40-50 per cent. of oil.

Pure "cold drawn" poppy oil is a pale golden yellow colour. Its specific gravity is .925, and its iodine value 134.

It is sun bleached for artists' use, and is extensively used for the preparation of artists' paints.

NIGERSEED OIL

This is obtained from the seeds of *Guizotia oleifera* grown in tropical Africa; it is of a pale yellow colour. Its specific gravity is about 0.925, and its iodine value (Wijs) about 132.

When the price allows, it is used as an adulterant of linseed oil, although its drying properties are very much less.

SUNFLOWER OIL

This oil, which has fairly good drying properties, is expressed from the seeds of the common sunflower, which is largely cultivated in Russia, China and India. It has a golden yellow colour and is sometimes used as a substitute for linseed oil.

Its specific gravity is 0.924, and its iodine value (Wijs) about 130.

LUMBANG OIL (CANDLENUT OIL)

This oil is obtained from the seeds of *Aleurites moluccana*, a tree which flourishes in the western tropics.

It has been used in America as a substitute for linseed oil in the manufacture of paints, but is not very satisfactory on account of its inferior drying properties, and also its tendency to darken on heating.

Its specific gravity at 15.5° is 0.925 and its iodine value (Wijs) is about 165.

RUBBER SEED OIL (PARA RUBBER TREE SEED OIL)

This oil is obtained from the seeds of the Para rubber trees (*Hevea brasiliensis*) a native of Brazil. It also has been suggested as a substitute for linseed oil, but on account of its very poor drying qualities it is quite useless for this purpose.

Of a pale yellow colour, its specific gravity is 0.923 and the iodine value about 115 (Wijs method).

CORN OIL OR MAIZE OIL

This oil is obtained from the germ of the Indian Corn (*Zea mais*). It is a clear golden yellow oil with a characteristically pleasant odour and taste. It is used in America for adulterating linseed oil, but its drying properties are very weak, and its use for this purpose is very unsatisfactory.

Its specific gravity is 0.925 at 15.5° C., and it has an iodine value of about 119 (Wijs method).

ROSIN OIL

When rosin is distilled in fire-heated stills (Fig. 33) into which superheated steam is passed, or even by means of superheated steam alone, five principal products are obtained, namely—

1. Gaseous matter	2.5	per cent.	} 150° C.
2. Acid water (acetic and formic acids)	2.5	„	
3. Rosin spirit	5.0	„	
4. Rosin oils (pale, blue and green)	85	„	200° C.
5. Pitch	5	„	350° C.

Rosin oil varies in colour and consistency from a thin fluid to one as thick as

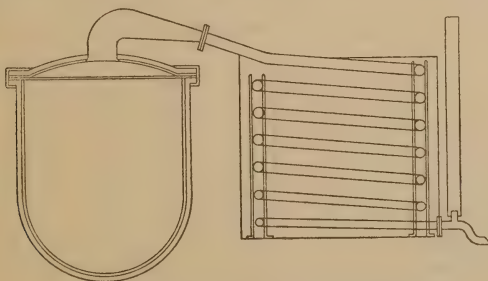


FIG. 33.—ROSIN STILL AND CONDENSING WORM.

symp. The earlier fractions are the palest in colour, lightest in density, and the most mobile.

The specific gravity varies from 0.92 to 1.030.

The cruder varieties have a bluish bloom or fluorescence, which becomes less marked after careful refining with caustic soda.

Rosin oils contain varying amounts of free rosin acids, which range from 9 to 30 per cent. according to the specific gravity of the oil.

Rosin oil, when exposed to the air, absorbs oxygen, and produces a glossy, hard, inelastic film; it is therefore sometimes used as an adulterant of linseed oil, especially in the manufacture of the so-called "boiled paint oils." Its presence is readily detected by the Liebermann-Storch test, and by the percentage of unsaponifiable matter.

CHAPTER XVII

SOLVENTS AND DILUENTS

PAINTS and varnishes always contain, as one of their essential constituents, a proportion of volatile bodies which act as solvents or diluents in order to reduce them to a suitable working consistency so that they may be readily applied.

The proportion of these volatile bodies varies considerably according to the nature of the medium to be thinned out, and also according to the viscosity required of the finished product.

For example, the proportion of volatile solvents needed to produce paints and varnishes suitable for application by spraying or dipping is naturally much greater than where these materials are applied by brushing.

The volatile constituents, in most cases, simply function as solvents or diluents, and after the application of the paint or varnish volatilise away, leaving the non-volatile constituents behind spread out evenly in the form of a thin film on the surface to which they have been applied.

In certain cases, however—and this is especially noteworthy as regards oil of turpentine—the solvent functions not only as a volatile medium, but also as an oxidising agent, inasmuch as it absorbs oxygen, whereby the oxidisable non-volatile constituents are oxidised more rapidly and completely to hard films; in addition, such solvents leave behind a small proportion of resinous material which acts as a binding agent.

The solvents in general use in the paint and varnish industries are very numerous, and their number is increasing year by year.

American turpentine is still by far the most valuable and highly esteemed of all the solvents that are in general use in the paint and varnish industries; though of late years, on account of its comparatively high price, it has been replaced to a considerable extent by turpentine substitutes consisting of petroleum distillates (mineral turpentine).

These petroleum distillates, although lacking in many of the valuable properties of turpentine, nevertheless may be considered to be of great value as solvents; their use increases year by year, and there is little doubt that the time will come when the natural supplies of turpentine will become so reduced that it will be completely replaced by these substitutes.

TURPENTINE

(Spirits of Turpentine, Oil of Turpentine, American Turpentine,
"Turps," Oleum Terebinthinæ.)

Turpentine, Gum Turpentine, Oil of Turpentine, and Spirits of Turpentine is the name variously given to a product which has long been used in the paint and varnish industries. It is obtained by the distillation of a concrete oleo-resin which exudes from various species of trees belonging to the Conifer.

The greater part of the American turpentine is obtained from the southern long yellow leaf pine (*Pinus palustris*). Approximately 75 per cent. of the world's supply of turpentine is produced in the United States, the remaining 25 per cent. being mostly obtained in the coastal regions of south-western France from the maritime or cluster pine (*Pinus pinaster* or *maritima*).

Small quantities of turpentine are also obtained in Spain and Portugal from the Spanish pine; in Greece and Algeria from the Aleppo pine (*Pinus halepensis*); in Northern India from the chir pine (*Pinus longifolia*); in Central Germany, Poland and Northern Russia from the Norwegian pine or Scotch fir (*Pinus sylvestris*).

The method used to secure the exuding concrete oleo-resin is to "box" the trees during the winter months by making incisions in the trunks of the coniferous trees about 1 to 2 ft. from the ground, so as to form a cavity into which the resinous exudation known as "gum thus" can flow. Each of these cavities or "boxes" has a capacity of about three pints, and sometimes as many as three "boxes" will be made in one tree. The trunk above the "box" is cut in several places in order to assist the flow. About March the sap begins to run and collect in the "boxes," and continues during the whole of the summer months.

The gum is collected from the boxes, emptied into barrels, and conveyed to the stills.

The method of distillation is practically the same to-day as it was fifty or sixty years ago. The apparatus consists of a large copper kettle of 500 to 1000 gallons capacity, connected by a removable still-head to a copper worm kept cool in a large tub of water. The stills are, as a rule, fire-heated, though sometimes superheated steam is now used.

From seven to fourteen barrels of gum are distilled at one operation. Water comes over with the turpentine at first; and afterwards a small stream of water is allowed to run into the still so that the turpentine distils off at a temperature lower than its boiling-point in a current of steam. The water and turpentine pass together into the receiver, and are separated and removed at different levels by suitably inserted pipes.

The yield of turpentine is about 25 per cent. of the charge, whilst the residue in the still consists of the rosin (colophony) of commerce. The latter is usually paler in colour when superheated steam is used in place of direct fire heat. The colour of the rosin residue is, however, also dependent on the nature and quality of the oleo-resinous exudation that is being distilled.

Properties and Uses

Turpentine, or "Turps," is a clear, water-white mobile liquid having a characteristic odour and taste.

Its specific gravity is 0.862 to 0.870 at 15.5° C. It boils at about 160° C. (320° F.) and almost entirely distills below 180° C. (356° F.), little or no residue remaining.

Turpentine is an essential oil, and consists almost entirely of the Terpene "Pinene," a hydrocarbon of the formula $C_{10}H_{16}$, which exists in two modifications α and β (it contains 72 per cent. α and 28 per cent β Pinene). American turpentine is dextro-rotary (+1° to +15°). In the presence of air it absorbs oxygen and becomes viscous; the oxygen so absorbed is readily transferred to other substances, so that this liquid, as has already been mentioned, acts in varnishes and paints not only as a solvent but also as an oxidising agent. Petroleum distillates, on the other hand, are inert, and do not act as oxidising agents, but promote the drying of paints and varnishes only by their greater or less volatility.

Turpentine is inflammable and burns with a smoky flame. It flashes at 94° F. It is soluble in its own volume of glacial acid, in ether, benzol, etc.

It is a good solvent for oils, resins and waxes, hence is largely used in the paint and varnish industries and in the manufacture of shoe polishes.



FIG. 34.—ABEL FLASH POINT APPARATUS.

Average Analytical Constants for American Turpentine

Specific gravity at 15.5° C.	. = 0.864
Flash point (Abel)	. = 94° F.
Refractive index at 15.5° C.	. = 1.468-1.478
Iodine value (Wijs)	. = 400
Boiling-point	. = 155° C.

SCHEME FOR THE ANALYSIS OF OIL OF TURPENTINE

1. Specific Gravity

The specific gravity is determined at 15.5° C. in a 50 c.c. gravity bottle (see Chapter XVI.).

2. Refractive Index

The determination is made at any convenient temperature with an accurate instrument, and the results calculated to 15.5° C., using the correction .00042 for each degree that the temperature of determination differs from 15.5° C.

3. Flash Point

The flash point of an oil or spirit is that temperature at which sufficient vapour is evolved to form with the air in contact with it an inflammable or explosive mixture. In the case of turpentine and those spirits which flash below 120° F. the determination is usually carried out in the standard Abel Flash Point Apparatus (Close test) (see Fig. 34). This apparatus consists of a metal cup of standard size provided with a gauge and a closely-fitting metal cover. The metal cover is fitted with a thermometer which dips in the liquid under test, and also a movable slide by which the cup can be opened or closed at will.

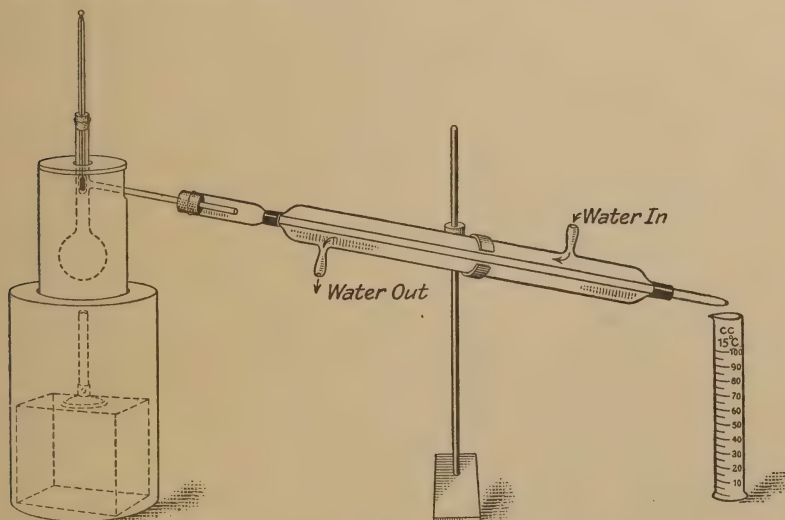


FIG. 35.—STANDARD DISTILLATION APPARATUS.

A small gas jet fixed on a pivot is made to dip into the opening at each degree rise of temperature, the action of opening the slide causing the flame to be applied.

The cup is heated by means of a bath of hot water at 130° F., and is filled with turpentine just up to the level of the gauge and the lid carefully pressed into position.

The small jet of gas is lit, and when the temperature reaches about 68° F. the slide is opened, which motion causes the jet to dip into the chamber.

The slide is opened and closed for each degree rise of temperature. The flash point is that temperature at which a large blue flame appears, and which spreads over the whole surface of the liquid and usually extinguishes the flame. A correction is necessary for atmospheric pressure, as the temperature of the flash varies 1.6° F. for each inch of the barometer.

4. Iodine Value

The iodine absorption of turpentine is carried out by the Wijs method in the manner described in the determination of the iodine value of linseed oil (Chapter XVI.).

Care should be taken to have an excess of 100 per cent. of iodine, and it is usual to perform the test side by side with a control specimen of pure turpentine.

5. Distillation Test

The most satisfactory test for ascertaining the purity of turpentine is to distil fractionally 100 c.c. in a standard Engler flask connected with a long condenser (see Fig. 35) and a graduated 100 c.c. receiving cylinder.

The distillation is performed as follows:—Carefully measure out 100 c.c. of the sample of turpentine in the 100 c.c. receiving cylinder and pour into the standard Engler flask (Fig. 36). Insert the cork provided with an accurate thermometer graduated from 0 to 400° C. at intervals of 1° C. and the marks numbered at every interval of 10° C.

The flask is connected with a glass condenser 60 cm. in length. The measuring cylinder may be used without drying as the receiving vessel for the distillate.

The flask is heated directly with a small Bunsen flame, which is carefully surrounded with an asbestos shield as a protection from draughts. The heat should be so regulated that the distillation proceeds at the rate of 5 c.c. per minute into the receiving cylinder.

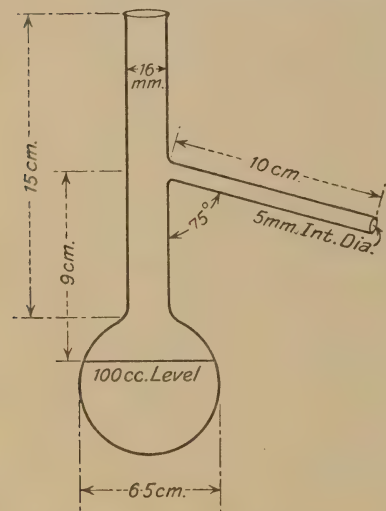


FIG. 36.—STANDARD ENGLER DISTILLATION FLASK.

The temperature at which the first drop leaves the lower end of the condenser is considered the initial boiling-point. Readings of the quantity in the receiver are taken when the next 10° point is reached, and for every 10° thereafter.

The distillation is continued until the point is reached where the last drop is vaporised and the bottom of the flask is dry.

If desired the various fractions may be kept separate and their specific gravity and refractive index taken.

Distillation in Steam.—Another method of conducting the distillation is to use steam, and thus altogether avoid direct heating. By this method any chance of the decomposition of the heavier fractions is avoided.

6. Polymerisation

(a) Take 20 c.c. of concentrated sulphuric acid in a graduated narrow neck flask. Cool and slowly run in drop by drop 5 c.c. of the turpentine to be tested with shaking.

Great care must be taken that the temperature of the mixture does not rise above 60° C.

After half an hour warm on a water bath to about 70° C., shaking well at intervals.

Cool to room temperature and add concentrated sulphuric acid till the unpolymerised portion rises into the graduated neck. Read the amount of the unpolymerised portion; separate and note its odour, colour, etc.

(b) *Oxidation by Fuming Nitric Acid.*—Put 30 c.c. of fuming nitric acid in a 100 c.c. flask and cool in a freezing mixture. Add 10 c.c. of the sample of turpentine from a burette drop by drop with continuous agitation. When the reaction is over pour into a graduated cylinder and read off the volume of the unattacked portion.

American turpentine as shipped from the States is hardly ever adulterated, and although the author has tested many thousands of such deliveries he has never been able to detect any of the various adulterants, such as petroleum distillates, benzoles, rosin spirit, chlorinated hydrocarbons, etc., which figure so largely in the various text-books dealing with this subject.

In some cases no doubt the true gum turpentine or spirits of turpentine may be mixed with a proportion of wood turpentine (see overleaf), but as this product, when carefully prepared, has the same chemical and physical constants as the genuine article distilled from the oleo-resin, its detection by the usual analytical methods is impossible. If present, however, in a greater proportion than 10 per cent. its presence is readily indicated by its peculiar woody empyreumatic odour.

Specification for American Oil of Turpentine

(1) The turpentine must be a volatile oil distilled from the resinous exudation of the live pine (*Pinus palustris* and other species of pine) unmixed with any other substance such as wood turpentine, petroleum distillates, etc. It must be clear and colourless, and free from water and sediment, and possess a characteristic odour.

(2) Three drops allowed to fall on a piece of white filter paper must completely evaporate at a temperature of 70° F. without leaving a stain.

(3) When 100 c.c. of the material are distilled from a standard Engler flask of 100 c.c. capacity, under a pressure of 760 mm. of mercury, and at the rate of not less than 3 c.c. nor more than 4 c.c. per minute, not less than 70 c.c. should distil at or below 160° C., and not less than 90 c.c. at or below 170° C.

(4) The specific gravity of the material at 15.5° C. must not be less than 0.862 nor greater than 0.872.

(5) The flash point (close test) must not be below 90° nor above 100° F.

(6) When 10 gms. of the turpentine, contained in an open dish, is maintained

at a temperature of 212° F. for two to three hours, the residue must not exceed 2 per cent.

(7) The refractive index shall not be less than 1.46 nor more than 1.478 at 15.5° C.

A typical sample of genuine American turpentine tested by the author gave the following results :—

Specific gravity at 15.5° C.	0.864
Flash point (Close test)	94° F.
Refractive index at 15.5° C.	1.470
Commences to distil at	156.5° C. (B.P.)
160° C.	75.4 per cent.
170° C.	94.0 "
180° C.	98.0 "
190° C.	99.0 "
200	all over
Residue	nil

WOOD TURPENTINE

The growing scarcity of genuine gum turpentine has caused the American producers to turn their attention to the manufacture of turpentine from the resinous wood of pine trees. This product is known as "wood" turpentine.

Wood turpentine may be extracted with volatile solvents, by steam, or by destructive distillation.

The manufacturers of wood turpentine now produce a product that comes within the accepted physical and chemical limits of gum turpentine, though the smell of this product may be readily distinguished from that of the characteristic smell of genuine gum turpentine.

Wood turpentine is as a rule obtained by two methods. The usual process is by the destructive distillation of the branches or the roots of the pine or mill waste whereby the turpentine thus obtained has an empyreumatic or pungent woody odour, due to the decomposition products from the breaking down of the rosin and the wood which renders the refining of the turpentine a difficult matter.

The other process of obtaining wood turpentine is by the steam distillation of the chipped stumps or mill waste whereby any serious decomposition of the wood or rosin is avoided. On redistillation the wood turpentine thus procured has a pleasant odour suggestive of pine wood ; and the constants come within the accepted physical and chemical limits of gum turpentine.

Analysis

The valuation of a wood turpentine is carried out in exactly the same manner as already described under the analysis of gum turpentine. If the product possesses a nasty pungent woody smell, and contains over 10 per cent. of heavier fractions (pine oils) it should be rejected as being unsuitable.

A typical sample of a genuine crude wood turpentine on analysis gave the following results :—

Specific gravity at 15.5° C.	0.867
Flash point (Close test)	97° C.
Commences to distil at	156° C.
160° C.	3 per cent.
170° C.	55 "
180° C.	75 "
190° C.	90 "
200° C.	95 "
210° C.	96 "
Residue	4 "

FRENCH TURPENTINE

This variety is obtained by the distillation of the resinous exudation from the maritime pine (*Pinus maritima*, *Pinus pinaster*) which grows extensively in the South-West of France.

The process in use is very similar to that in America and need not therefore be described in detail.

Properties and Uses.—The properties of French turpentine are very similar to those of American turpentine, and it may be used in every case in place of the latter product.

French turpentine is lævo-rotatory (−18 to −40) whereas the American variety is dextro-rotatory.

It consists almost entirely of the Terpene "Pinene" ($C_{10}H_{16}$) containing about 63 per cent. α Pinene and 37 per cent. β Pinene.

It may be readily distinguished from American gum turpentine by its characteristic sweet smell.

The great bulk of the French turpentine is consumed in France, and only a small proportion is shipped to this country.

RUSSIAN TURPENTINE (SWEDISH TURPENTINE)

Russian turpentine is obtained by the distillation of the wood from the Norwegian pine or Scotch fir (*Pinus sylvestris*).

It consists mainly of the terpenes cinene and sylvestrine; hydrocarbons of the formula $C_{10}H_{16}$, and only a very small quantity of pinene. Russian turpentine is dextro-rotatory. It resembles American in many of its properties; it is, however, more variable in its composition and has a greater range of distilling temperature.

It is noteworthy on account of its characteristic nasty odour, which produces nausea and headaches, and renders it quite unsuitable for use in paints and varnishes.

Deodorisation of Russian Turpentine

Owing to its rank unpleasant smell many patents have been taken out for its deodorisation. The usual process, on the commercial scale, is as follows :—

The crude turpentine is churned in revolving wooden barrels for eight hours with about 5 per cent. of concentrated sulphuric acid. A considerable residue of black tarry matter separates out after this operation, and is drawn off.

The treated turpentine is next churned for three hours with a strong solution of caustic soda to remove all traces of acid. The turpentine is then pumped into stills and distilled over in the presence of caustic soda by means of superheated steam.

Another process consists in distilling the crude Russian turpentine in the presence of about $\frac{1}{2}$ per cent. of metallic sodium by the aid of superheated steam.

In both cases a thick resinous mass is left behind in the still.

The pure oil of turpentine thus obtained has a characteristic fairly sweet pleasant odour, but, unfortunately, no process has as yet been discovered whereby the crude Russian turpentine can be permanently sweetened to such a degree that it can be used in place of American or French turpentine.

The examination of a genuine Russian turpentine by the author gave the following results :—

Specific gravity at 15.5° C.	0.864
Flash point (Close test)	98° F.
Commences to distil at	154° C. (B.P.)
160° C.	2 per cent.
170° C.	64 "
180° C.	90 "
190° C.	96 "
200° C.	98 "
Residue	2 "

A sample of Swedish sulphite turpentine gave the following figures on examination :—

Specific gravity	0.862
Optical rotation	7° 30
Refractive index	1.4750 to 20°
Boiling point	159°
Distils between 160–170°	66 per cent.
" " 170–180°	28 "
" above 180°	6 "

PORTUGUESE TURPENTINE

Small quantities of turpentine are obtained from Spain and Portugal from the Spanish pine in a similar manner to French turpentine. Shipments of this product are occasionally made to this country; but the bulk is used for home consumption.

Portuguese turpentine is very similar in its properties to French and American turpentine, and may be used in their place.

A typical sample of Portuguese turpentine on analysis by the author gave the following results :—

Specific gravity at 15.5° C.	0.864
Flash point (Close test)	94° F.
First drop at	155° C.
160° C.	78 per cent.
170° C.	94 "
180° C.	96 "
190° C.	98 "
200° C.	dry
Residue	<i>nil</i>

"REGENERATED" TURPENTINE

This is a product of synthetic camphor manufacture. It has a peculiar camphor-like smell and is sometimes used as a solvent in place of turpentine. Its boiling point, 170° C., is considerably higher than that of turpentine.

TEREBENE (Terebenum).

This body is a mixture of dipentene and other hydrocarbons obtained by agitating oil of turpentine with successive quantities of sulphuric acid until it no longer rotates the plane of a ray of polarised light, and then distilling in a current of steam.

It is a colourless liquid having an agreeable odour and an aromatic taste (Sp. Gr. 0.862 to 0.866). It does not rotate the flame of a ray of polarised light, and should distil between 312.8° F. and 356° F. (156° C.–180° C.), leaving only a slight viscid residue (absence of resin).

Not more than 15 per cent. should distil below 329° F. (165° C.). This body should not be confused with terebine, which is a liquid drier (see Chapter XX.).

TURPENTINE SUBSTITUTES

(Petroleum Distillates, White Spirit, Benzine, Mineral Turpentine.)

The rapid depletion of the turpentine forests and the consequent high price of turpentine has resulted in the paint and varnish manufacturers making use of cheaper volatile solvents which are capable of replacing entirely, or in part, the turpentine they used.

The chief substitute for turpentine is a distillate of petroleum, commonly known as "white spirit" (benzine in America), enormous quantities of which are now used in the paint and varnish industries.

Great controversy has arisen as to the respective merits of these petroleum distillates as compared with turpentine, some manufacturers of white spirit claiming that their product is equal in all respects to that of turpentine, and capable of

replacing this body as a solvent for all purposes for which it is commonly used in the manufacture of paints and varnishes.

This view, in the opinion of the author, is quite erroneous, as turpentine is by far the best solvent for all oleo-resins, and, as has already been mentioned, it is not only superior as regards its solvent properties, but in addition it increases the speed of drying of the paint and varnish with which it is mixed both by evaporation and by oxidation, and also acts as a bleaching agent on the oil, rendering the paint and varnish on drying whiter and paler in colour.

Moreover, paints and varnishes made with turpentine and applied to bare wood are, owing to their superior solvent properties, able to penetrate the more or less resinous surface of the wood better than in those cases where white spirit is used; thus producing a flat or semi-flat surface on which the succeeding coat of paint or varnish can "key" on without showing any tendency to peel, run, or shell off ("Sissing" of Varnishes, see Chapter XVIII.).

Varnishes made on turpentine and tanked, body up and come to maturity much more quickly than those made with white spirit; the gloss also of these varnishes is much superior and does not show the objectionable tendency to "bloom" or go flat which so often happens in the case of varnishes made on white spirit.

For these reasons it is more satisfactory when white spirit is used to mix it with about 25 per cent. of genuine turpentine in order to obtain the best results.

MANUFACTURE OF WHITE SPIRIT

The crude material from which white spirit is obtained is petroleum or rock oil. The distribution of petroleum is world-wide. The chief areas worked at the present day are America (Pennsylvania, California, Mexico, etc.) Europe (Russia, Roumania, etc.) and Asia (Burmah, Borneo, Persia, Java, etc.).

When petroleum is distilled three main products are obtained, viz.: (1) light oils, (2) burning oils, (3) lubricating oils.

In addition to these oils two other valuable by-products are obtained, viz.: vaseline or petroleum jelly and petroleum pitch.

AMERICAN PETROLEUM

The petroleum which gushes out from the oil wells of America after boring operations is a very crude material, and varies considerably according to the locality from which it is obtained. It is subjected to a distillation process whereby the various fractions are separated, and the products thus collected are refined by treatment either with sulphuric acid and then with caustic soda, or else by means of Fuller's earth, bauxite or other processes, for details of which the reader is referred to special treatises dealing with the subject, which is outside the scope of this book (see Bibliography).

American petroleum on distillation yields the following products.

(1) *Light Oils* (B.P. 0° C.–150° C.)

	B.Pt.
(a) Cymogene	0° C.
(b) Rhigolene	18.3° C.
(c) Benzine	45–60° C.
(d) Petroleum ether	70–90° C.
(e) Ligroin	120–130° C.
(f) Petrol, gasoline and benzoline	70–120° C.
(g) Naphtha	90–130° C.

(2) *Burning Oils—Kerosene*

Kerosene, or lamp oil, boils at from 150°–300° C. As a rule it is a colourless liquid possessing a peculiar smell, which varies enormously according to the refining process which it has undergone. Its specific gravity is about 0.820 and its flash point varies from 90° F.–120° F.

(3) *Lubricating Oils*

The distillation products of the crude petroleum obtained in Russia, Roumania, Borneo and Java may also be sub-divided into three main groups in a similar manner to those of American petroleum, although the yields and composition of the various fractions of course varies considerably according to the locality from which the crude oil is obtained.

WHITE SPIRIT

The starting point in the manufacture of white spirit is a petroleum fraction which is intermediate between the light oils and the burning oils.

This distillate has, as a rule, a specific gravity from about 0.798 to 0.811, and flashes at a temperature roughly between 74° F. to 95° F. This petroleum fraction is pumped into large copper or iron stills heated by superheated steam or sometimes by direct fire heat, though in this case the distillate obtained is not so sweet as in the case where superheated steam is employed.

The stills are provided with dephlegmators in order to get a better or more even separation of the fractions, and the distillation is conducted, as a rule, under reduced pressure.

As the distillation proceeds more crude petroleum is sucked into the stills to replace the portion that has distilled over. The first portions that distil over are the lighter fractions, which are put to one side to be used as motor spirit.

The fractions distilling over between 150° C. and 250° C. are collected, bulked together, and again redistilled, while the residue in the still is used as fuel oil.

The petroleum fraction which has been bulked together and subjected to a redistillation process is usually separated into three fractions, viz., light, medium, and heavy white spirit, and is put on the market under the general name of white spirit, the paint and varnish manufacturer selecting the particular grade that best suits his requirements.

The white spirits thus obtained vary very considerably as regards the sweetness of their odour, and as this is a factor of great importance when used as a turpentine substitute it is necessary in the case of those spirits which have a pungent unpleasant odour to deodorise them. Many deodorising processes are in use, such as the treatment with solutions of hypochlorite of soda, bleaching powder, Fuller's earth, and so on.

The smell is, as a rule, due to the presence of sulphur compounds and varies enormously according to the crude petroleum which has been used; the Roumanian crude petroleums yielding white spirits having a distinctly pleasant sweet smell, while those obtained from the crude petroleum from Ohio and Texas are distinctly objectionable.

Properties and Uses.—White spirit, used as a turpentine substitute, should be a colourless mobile liquid having a pleasant odour. It should be free from grease, and on evaporation on a water bath at 100° C. should leave no residue.

Its specific gravity should be about 0.800 and its flash point should be not less than 79° F. nor more than 97° F. It should distil between 150° C. and 250° C. The iodine value as distinct from that of turpentine is very small.

White spirit differs in composition according to the petroleum from which it is derived, and as it is a solvent composed of a large number of compounds, such as paraffin, olefine, and benzine hydrocarbons, the members of which so closely resemble each other in their chemical and physical properties, the simplest method of securing an approximate separation is by means of distillation.

At the present time white spirit is used in enormous quantities as a solvent or thinner in the paint and varnish industries; it is used also as a solvent in polishes, and as a cleaning spirit.

Scheme for the Analysis of White Spirit

In the selection of a white spirit for use as a substitute for turpentine, it is necessary to test carefully the various spirits offered as regards their odour, and to select only those that have a pleasant and sweet smell and are free from any objectionable paraffin or crude petroleum-like odour.

The spirit must be water-white in colour, and free from any yellowish cast or sign of a bloom.

Solvent Strength.—The solvent strength of white spirit varies considerably, and as a general rule the heavier fractions show greater solvent properties than the lighter ones.

The solvent strength may be determined by dissolving 10 parts of mixed fused calcium lead resinate in 90 parts of the various samples of white spirits, and standing the solution in ice cold water along with a standard 10 per cent. solution of calcium lead resinate in turpentine.

Those samples that separate after thirty-six hours should be rejected as being deficient in solvent power.

The gravity, flash point, and distillation figures are obtained in a similar way to what we have described under turpentine (see pp. 196–198).

Volatility Test.—To test the quickness of drying of a spirit and its freedom from grease, three drops should be poured on to a piece of filter paper and the time noted for it to completely evaporate as compared with the standard sample.

No greasy stain should be apparent on the paper after the complete evaporation of the spirit.

Distillation Test.—This test is carried out in the Standard Engler Distillation Apparatus in precisely the same way as in the case of turpentine (see page 198).

Specification for White Spirit

(1) The white spirit must consist wholly of a distillate of petroleum, water white, neutral, clear and free from water. It must be sweet and free from any objectionable odour.

(2) It must not flash (Close test) below 79° F. and not above 97° F.

(3) The specific gravity of the spirit at 15·5° C. shall be about 0·800.

(4) When 10 c.c. of the material are put in a glass crystallising dish 2½ in. in diameter and placed in a steam bath for 2½ hours the residue must not exceed 0·2 per cent. by weight.

(5) When 100 c.c. are distilled from a standard Engler flask of 100 c.c. capacity under a pressure of 760 mm. of mercury, the first drop must issue from the condenser at a temperature not below 140° C., and 99 per cent. must distil below 220° C.

The following distillation figures obtained by the author for various commercial white spirits used as turpentine substitutes will indicate clearly the composition of such bodies :—

	No. 1 Grade, White Spirit. ¹	No. 2 Grade, Light.	No. 3 Grade, Heavy.	No. 4 Grade, Extra Heavy.
Specific Gravity at 15·5° C.	0·8006	0·786	0·809	0·813
Flash point (Close test)	81° F.	79° F.	96° F.	141° F.
Boiling point (1st drop over)	145° C.	130° C.	160° C.	184° C.
150° C.	3 p. cent.	7 p. cent.
160° C.	21 "	35 "
170° C.	51 "	58 "	5 p. cent.	..
180° C.	70 "	77 "	65 "	..
190° C.	84 "	89 "	73 "	6 p. cent.
200° C.	92 "	95 "	85 "	8 "
210° C.	99 "	99 "	90 "	28 "
220° C.	100 "	100 "	95 "	62 "
230° C.	98 "	84 "
240° C.	99 "	94 "
250° C.	95 "
Residue	1 "	5 "

¹ Standard grade of white spirit used as a turpentine substitute in varnish manufacture.

The following figures were obtained by the author on distilling a standard No. 1 Grade White Spirit mixed with varying percentages of genuine American gum turpentine, and are interesting as illustrating the effect produced by such additions on the temperature at which the various fractions distil over :—

	A No. 1 Grade White Spirit.	B A + 25% American Turpentine.	C A + 50% American Turpentine.	D A + 75% American Turpentine.	E Genuine American Turpentine.
Specific gravity at 15.5° C.	0.800	0.816	0.832	0.848	0.864
Flash point (Close test)	81° F.	82° F.	84° F.	87° F.	94° F.
Boiling point	147° C.	147° C.	147° C.	147° C.	156° C.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
150° C.	3	3	3	3	..
160° C.	32	24	22	28	75
170° C.	44	66	78	89	98
180° C.	76	85	90	94	99
190° C.	89	92	94	97	dry
200° C.	94	97	98	98	..
210° C.	99	99	99	99	..
215° C.	99.5	100	100	100	..
220° C.	dry

CAMPHOR OIL

The volatile oil which is obtained from the camphor laurel (*Laurus camphora*)—which grows principally in Japan—by a process of steam distillation is redistilled to separate out all the camphor, and the residual oil is known commercially as camphor oil.

It is a colourless liquid with a camphor and eucalyptus like smell, and burns with a bright smoky-like flame. It has a specific gravity of about 0.875 and flashes at 97° F.

A distillation of a sample of heavy camphor oil by the author gave the following results :—

B.P.	210 per cent.
220° C.	24 „
230° C.	50 „
240° C.	90 „
250° C.	99 „
Residue	1 „

It possesses fairly good solvent properties and is sometimes used as a substitute for turpentine.

ALCOHOL (ETHYL ALCOHOL)

Ethyl alcohol (C₂H₅OH) is prepared on a technical scale in the spiritous fermentation of saccharine juices. Pasteur considered that during fermentation

94 to 95 per cent. of the sugar changes to alcohol and carbonic acid, according to the following equation :—



Fusel oil (chiefly amyl alcohol $\text{C}_5\text{H}_{11}\text{OH}$), some glycerol $\text{C}_3\text{H}_8\text{O}_3$ (2–5 per cent.) and succinic acid $\text{C}_4\text{H}_6\text{O}_4$ (0·6 per cent.) are formed simultaneously, although the latter two appear generally towards the end of the fermentation.

The material used in the preparation of alcohol by means of fermentation are saccharine plant juices and starch containing substances such as the seeds of grain and potatoes.

Manufacture of Potato Spirit

The potatoes are heated with steam to 140–150° C. under pressure of from 2–3 atmospheres, and the potato mash thus formed is digested at 57–60° C. in a mashing apparatus with finely divided malt containing water. In this manner the starch of the potatoes is converted into sugar. The mash is then run into fermentation tubs, where it comes in contact with “pure culture” artificial yeast and is then fermented. Crude spirit results from the distillation of the fermented mass.

Manufacture of Pure Absolute Alcohol

To purify further the crude spirit it is fractionated in a special column distillation apparatus whereby a spirit containing 95 per cent. of alcohol is obtained. The last fractions or “tailings” which come over contain large quantities of fusel oil.

To prepare anhydrous alcohol the rectified spirit (90–95 per cent. alcohol) is distilled and redistilled with ignited quicklime till all traces of water are removed.

RECTIFIED SPIRITS OF WINE

(Spiritus Vinus Rectificatus.)

The alcohol ordinarily met with in commerce is known as “rectified spirits of wine” or “rectified spirit.” It contains 90 parts by volume of alcohol and 10 parts by volume of water. Its specific gravity is 0·8337 at 15·6° C.

METHYLATED SPIRITS

Mineralised methylated spirits sold by licensed retailers for general use (except, of course, as a beverage or medicine) is a mixture of 90 parts of rectified spirits of wine with not less than 10 parts of approved wood naphtha plus $\frac{1}{2}$ per cent. of petroleum; and this mixture, which is thus rendered non-potable, is allowed by the Excise authorities to be sold for domestic purposes free of duty.

Methylated spirit is sold at the strength of 64° O.P. (“over-proof”) and has a specific gravity of 0·8221. It contains 90 per cent. of alcohol.

INDUSTRIAL SPIRIT

As this denaturing process renders the alcohol unfit for many industrial purposes the Excise authorities allow an "Industrial" spirit to be used under special regulations; this consists of a mixture of 95 per cent. rectified spirits of wine and 5 per cent. of approved wood naphtha.

Properties and Uses.—Pure alcohol is a mobile colourless liquid with an agreeable characteristic odour. Its specific gravity at 15.5° C. is 0.7939; boiling point 78.3° C. It burns with a pale blue flame, which is scarcely luminous. It is very hygroscopic and mixes in every proportion with water. The mixture takes place with disengagement of heat, and there is a contraction after cooling. The maximum contraction is reached when one molecule of alcohol is mixed with three molecules of water, corresponding to the formula $C_2H_5OH + 3H_2O$.

The amount of absolute alcohol in a given sample of commercial alcohol is determined from its specific gravity by the aid of a table of percentages, or by using specially constructed hydrometers (alcoholometers), which show the percentage of alcohol by direct reading.

Ethyl alcohol forms crystalline compounds with some salts, like calcium chloride and magnesium chloride. It plays the part of water of crystallisation in them. When subjected to the action of oxidising agents, such as manganese peroxide and sulphuric acid, chromic acid and air, it is converted into acetaldehyde (CH_3COH) and acetic acid (CH_3COOH).

Bleaching powder changes alcohol into chloroform, and iodine and caustic potash convert it into iodoform.

Alcohol dissolves fatty acids and castor oil readily, but it has only a slight solvent action on the other fatty oils. It is a first-rate solvent, and readily dissolves rosin and other resins such as sandarac, shellac, mastic, etc. It is very extensively used in the form of methylated spirits in the manufacture of French polishes and spirit varnishes.

SYNTHETIC ALCOHOL

The synthetic production of alcohol from acetylene was largely developed in Germany during the war. The acetylene obtained from calcium carbide was converted into aldehyde in the presence of a catalyst such as a mercury salt; the aldehyde thus formed was reduced to alcohol by passing its vapour, mixed with hydrogen, over finely divided nickel at a definite temperature.

Methylated Finish is methylated spirit containing about 3 ozs. of rosin to the gallon. It is chiefly used by French polishers for making up their own polish, as the Excise authorities do not place so many restrictions on its sale.

METHYL ALCOHOL

(Wood Alcohol, Wood Naphtha, Wood Spirit.)

Methyl alcohol CH_3OH is obtained by the dry distillation of wood for making acetic acid. The crude wood vinegar contains about 3 per cent. of wood spirit, which is

removed by neutralising the acid and separating the alcohol by fractional distillation. The crude wood spirit thus obtained contains acetone as its chief impurity.

Methylalcohol is, when pure, a colourless mobile liquid, with a strong characteristic smell. It boils at 66–67° C. and has a specific gravity of 0.796. It mixes with water, alcohol and ether. It is readily inflammable and burns with a non-luminous flame.

Wood alcohol is a more powerful solvent than ethyl alcohol and is used to a limited extent in the manufacture of spirit varnishes. Owing to its toxic properties care must be taken to see that efficient ventilation is provided wherever it is used.

AMYL ALCOHOL ($C_4H_9CH_2OH$)

(Fusel Oil.)

Fusel oil which is obtained in the distillation “tailings” of alcohol consists chiefly of amyl alcohol (isobutyl carbinol).

It is obtained pure by adding water, redistilling, and collecting the fraction boiling at 129–132° C.

Amyl alcohol is a colourless, mobile liquid possessing a characteristic, unpleasant smell; its vapours are very pungent and irritating.

It rotates the flame of polarisation to the left. Its specific gravity is 0.8184, and it boils at 132° C.

Fusel oil was formerly very extensively used in the manufacture of transparent lacquers owing to its excellent solvent properties, but it has been displaced in recent years owing to its unpleasant smell and toxic effects.

NORMAL BUTYL ALCOHOL

$CH_3(CH_2)_2CH_2OH$; B.P. 116° C.; Specific gravity at 20° C. 0.8099

is now also used as a solvent for spirit varnishes and lacquers on account of its excellent solvent properties.

ACETONE (CH_3COCH_3)

(Dimethyl Ketone.)

Acetone is prepared by the distillation of calcium or barium acetate or from crude wood spirit.

It is a mobile, colourless liquid, with a characteristic odour. Its specific gravity is 0.814 and boiling point 56.5° C.

It is miscible with water, alcohol and ether. Acetone is very inflammable, and burns with a bright flame. It is an excellent solvent and is very largely used, alone or mixed with alcohol and benzol, as a solvent for resins, celluloid, cellulose nitrate and acetate (see Dopes, Chapter XIX.). It is also used as one of the chief ingredients in patent paint removers.

Mixed Ketones, such as methyl ethyl ketone, methyl propyl ketone, etc., made by the distillation of the barium salts of the corresponding acids with barium acetate, are also used at the present time as a substitute for acetone in the manufacture of dopes and celluloid varnishes.

ETHER

(Ethyl Ether ($C_2H_5)_2O$, Sulphuric Ether.)

Ether is made from ethyl alcohol and sulphuric acid heated to $140^{\circ}C$. The process is a continuous one, alcohol being constantly added.

It can also be made from benzine, sulphuric acid, and alcohol at $135-145^{\circ}C$.

Anhydrous ether is obtained from ordinary ether by shaking with water to remove the alcohol and distilling over quicklime or chloride of calcium, and drying it finally with sodium wire until there is no further evolution of hydrogen.

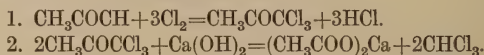
Ether is a mobile liquid with a characteristic smell, and its specific gravity at $0^{\circ}C$ is 0.736. It is an anæsthetic. It boils at $35^{\circ}C$., and evaporates very rapidly even at medium temperatures.

It is extremely inflammable, burning with a luminous flame, and its vapour mixed with air explodes on ignition.

It is miscible with alcohol and dissolves in 10 parts of water. Owing to its powerful solvent properties it is used as a vehicle for dissolving many organic substances.

CHLOROFORM ($CHCl_3$)

Chloroform is prepared technically by treating alcohol or acetone with bleaching powder. The bleaching powder is made into a thin paste with water and mixed with the acetone. Gentle heat is applied till a reaction sets in, which is indicated by the frothing of the liquid. The chloroform distils over, and as the reaction subsides heat is applied to complete the distillation. The course of the reaction may be expressed by the following equations:—



Chloroform is a colourless liquid of an agreeable ethereal odour and sweetish taste. It solidifies in the cold and melts at $-62^{\circ}C$. It is readily volatile, and is largely used as an anæsthetic and also, to a lesser extent, as a solvent for oils and waxes.

CARBON BISULPHIDE (CS_2)

Carbon bisulphide is prepared commercially by passing sulphur vapour over red-hot charcoal. In the manufacturing process the charcoal is heated in vertical cast-iron retorts set in a suitable furnace. The heat of the furnace also melts the sulphur, which is placed near the base of the retorts; the sulphur vapours rise through the red-hot charcoal and form carbon bisulphide, which escapes at the top. The carbon bisulphide is condensed in 30-ft. long condensing coils.

The crude product is purified by repeated distillation.

Carbon bisulphide is a colourless, mobile liquid with a peculiar, offensive smell (when absolutely pure its odour is very faint). Its specific gravity at $0^{\circ}C$ is 1.297. It is a very volatile and poisonous liquid and readily burns with a blue flame.

It is an excellent solvent for iodine, sulphur, fatty oils and resins, and is used in vulcanising india-rubber.

CARBON TETRACHLORIDE (CCl_4)

Carbon tetrachloride is prepared by the action of chlorine on carbon bisulphide. It is a pleasant-smelling colourless liquid, boiling at 76°C . Its specific gravity at 0°C . is 1.631. Owing to its excellent solvent properties it is largely used for dissolving oils, fats and resins. It is non-inflammable, and hence can be used in place of very highly inflammable and dangerous solvents such as ether acetone and carbon bisulphide.

AMYL ACETATE ($\text{C}_5\text{H}_{11}\text{C}_2\text{H}_3\text{O}_2$)

Amyl acetate is obtained by distilling potassium acetate with amyl alcohol and sulphuric acid. It is a colourless, mobile liquid having a specific gravity of 0.896. It has a pleasant pear-like odour, and is chiefly used as a solvent for gun cotton in the manufacture of nitro-cellulose varnishes. It boils at 137°C .

Butyl Acetate, the properties of which closely resemble those of amyl acetate, is also frequently used as a solvent for gun cotton in place of amyl acetate.

ROSIN SPIRIT

In the distillation of rosin about 10 per cent. of crude rosin spirit is obtained (see p. 193), which has a darkish brown colour.

It is purified by agitation with caustic soda solution and subsequent redistillation.

Rosin spirit is a water-white mobile liquid with a characteristic sharp terpene-like odour. Its specific gravity varies from 0.86 to 0.891, and it flashes at about 100°F .

In composition rosin spirit is a mixture of several hydrocarbons, such as the paraffins, olefines, etc., and varies according to whether it has been obtained by steam or fire distillation.

It boils at about 117°C ., and should all distil over below 260°C .; any higher boiling point fractions indicate the presence of rosin oil, which is objectionable, as it would retard the drying properties of the spirit.

Rosin spirit is largely used as a solvent, and but for its pungent smell would make a good substitute for turpentine.

SHALE SPIRIT OR SHALE NAPHTHA

Shale spirit is obtained by the destructive distillation of bituminous shale. Large deposits of shale are found in Scotland, and this material is subjected to a process of distillation at about 800°F . in large vertical retorts. The chief products obtained are :—

1. Shale Spirit. S.G. .66--75.
2. Paraffin Oils. S.G. .76--83.
3. Lubricating Oils.
4. Paraffin Wax.

A proportion of gaseous and tarry matter is also evolved, and a residue of coke is left in the still.

The crude oily fractions that come over contain a lot of tarry matter, and are treated first with sulphuric acid and then with caustic soda and again distilled.

The first fractions that come over constitute the shale spirit or shale naphtha of commerce.

Shale spirit is a water-white mobile liquid having a pungent characteristic smell which is rather unpleasant. Its specific gravity varies from .66-.75 and it boils at about 65° C. Its flash point is about 60° F.

Shale spirit is a complex mixture, and consists chiefly of paraffins and olefines. It is a good solvent and volatilises very quickly; it is largely used as a thinner for quick-drying anti-corrosion paints and in anti-fouling compositions.

BENZENE, BENZOL, COAL TAR NAPHTHA, SOLVENT NAPHTHA

In the manufacture of coal gas by the destructive distillation of coal large quantities of coal tar are produced, which, when subjected to a process of distillation, yield :—

1. Light oil (3-5 per cent.). B.P. up to 150°.
2. Middle oil (8-10 per cent.). B.P. from 150-210°.
3. Heavy oil (8-10 per cent.). B.P. from 210-270°.
4. Anthracene oil or green oil (16-20 per cent.). B.P. from 270-400°.
5. Residue—Pitch.

The light oils, when subjected to a process of fractional distillation, may be separated into the following bodies :—

Benzol or benzene	C_6H_6 .	B.P. 81°; S.G. at 0°=0.899.
Toluene	C_7H_8 .	B.P. 110°.
Xylene (o, m, p)	C_8H_{10} .	B.P. 138-141°.

Benzol or Benzene (C_6H_6) is a colourless liquid with a characteristic smell. It burns readily with a luminous smoky flame. It is an excellent solvent, and is used in the manufacture of lacquers and dopes and paint removers.

50 per cent. benzol is a mixture of benzene, toluene and xylene, of which 50 per cent. distils below 100° C.

90 per cent. benzol is a mixture of benzene, toluene and xylene, of which 90 per cent. distils below 100° C.

Solvent or Light Coal Tar Naphtha is a mixture of benzene hydrocarbons, and is largely used as a solvent in the paint, varnish and india-rubber industries.

It is a colourless liquid having a peculiar characteristic smell. Its specific gravity varies between 0.860 to 0.884, and as a rule 90 per cent. distils below 170° C.

BENZINE, PETROLEUM ETHER

Benzine—which must not be confused with benzene or coal tar benzol (C_6H_6)—is a light petroleum fraction obtained in the distillation of petroleum oil.

Its specific gravity is about .638-.660, and it boils at from 45-60° C.

Petroleum ether is a somewhat heavier fraction (B.P. 70-90° C.) and has a specific gravity of about .650-.660.

Both bodies are extensively used as solvents for oils, waxes, and in the dry-cleaning industry.

TERPINEOL ($C_{10}H_{17}OH$)

Terpineol is obtained when crystalline terpin is boiled with water and 1 per cent. of hydrochloric acid, and distilled. It is a colourless oily liquid with a peculiar fragrant odour like lilac. It is optically active and boils at 215° C.

Terpineol is an excellent solvent for medium-hard and soft copals, and only its high price prevents its more extended use in the varnish industry.

EPICHLORHYDRIN (CH_2Cl , CH , CH_2O)

Dichlorhydrin is obtained when anhydrous glycerine is mixed with an equal volume of glacial acetic acid saturated with hydrochloric acid gas, and distilled. When this body is treated with an aqueous solution of caustic potash, and distilled, epichlorhydrin is obtained.

The latter is a colourless mobile liquid with an ethereal smell. It has a specific gravity 1.203 at 0° C. and boils at 117°. It is an excellent solvent for all oils and resins.

The following chlorinated hydrocarbons are now extensively used as solvents for the extraction of oils from their seeds, and also in the manufacture of varnishes, dopes, lacquers and paint removers :—

$C_2H_2Cl_2$ Dichlorethylene.	Sp. Gr. 1.25.	Boiling Point	55° C.
C_2HCl_3 Trichlorethylene.	„ 1.47.	„	87° C.
C_2Cl_3 Perchlorethylene.	„ 1.62.	„	121° C.
$C_2H_2Cl_4$ Tetrachlorethane.	„ 1.60.	„	147° C.
C_2HCl_5 Pentachlorethane.	„ 1.70.	„	159° C.

CHAPTER XVIII

MANUFACTURE OF OIL VARNISHES

THE manufacture of oil varnishes is an industry which at the present time has assumed very great importance. Many hundreds of thousands of gallons are produced yearly in this country alone, which has long been famed for the excellence of its varnishes. In fact, the methods of manufacture used in America and the Continent are based on the English practice.

The varnish made in this country is exported to all parts of the world, and is still able, in spite of high tariff restrictions, to compete even in those countries which have large manufactories of their own, such as, for example, America and France.

The first known directions for making a linseed oil varnish were indicated by a monk named Theophilus so far back as the twelfth century. But for many years varnishes were made only in very small quantities by artists for their own personal use.

According to Livache the first varnish factory was started in England in 1790. Later, factories using processes based on English methods were established on the Continent and in America.

The composition of oil varnishes is comparatively simple, and consists simply of resin, drying oil and a volatile solvent. Nevertheless the manufacture of high-class varnish is an art that requires very long experience and an extensive knowledge of the various properties of the resins and oils that are necessary to produce a high-class product.

The various proportions in which the gums, or resins, and oils are "run," and the methods of working them up, together with the amount and character of the driers required in the different varnishes that are made, are regarded as valuable trade secrets, and consequently very jealously guarded. In many cases the processes in use are handed down from father to son, and it is not uncommon to find factories where the same family have been employed in the manufacture of varnishes over a long period of years.

Oil varnishes may be roughly divided into the following three classes :—

(1) *Inside Varnishes*, which comprise those varnishes which are not durable enough to withstand severe outside exposure and weathering influences, and are therefore only suitable for indoor use. As a rule they dry off quickly with a hard yet brittle, highly lustrous surface or "face." These varnishes are usually sold under the following designations :—

Inside copal varnish.

Furniture varnish.

Inside oak varnish.

Floor varnish.

(2) *Outside Varnishes*, which dry with hard, tough films, and are extremely durable, wear well and keep their gloss for a long period even under exposure to severe weathering influences. The following varnishes are comprised under this classification:—

Durable or finishing body varnish for coach and motor work.

Finishing carriage varnish and hard drying carriage varnish.

Outside oak varnish or elastic oak varnish.

Coburg varnish, and others.

(3) *Stoving Varnishes*, which are chiefly used in metal work and in the tin-printing trades.

They require to be stoved for a few hours at a temperature of about 150–250° F., when they dry off, giving extremely hard and tough films.

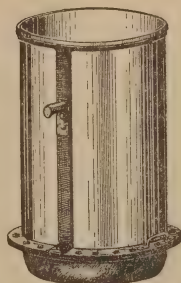


FIG. 37.—60-LB. GUM RUNNING POT; ALUMINIUM TOP WITH FLANGED-ON DETACHABLE COPPER OR SPECIAL BRONZE BOTTOM.

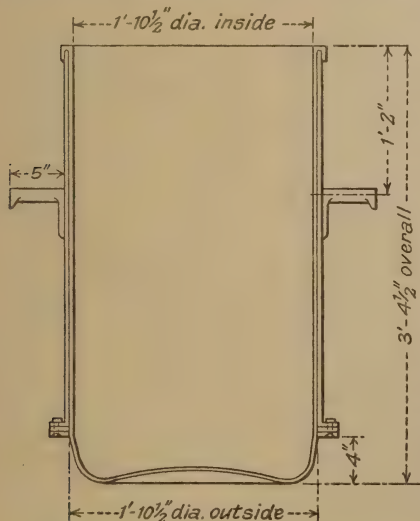


FIG. 37A.—STANDARD 60-LB. ALUMINIUM GUM POT, SHOWING DIMENSIONS.

The plant used in the manufacture of varnishes is comparatively simple, and whilst, of course, modifications exist in different factories, and the methods of working vary considerably, yet in the main essentials the plant and processes are the same.

PLANT AND PROCESSES

The gums or hard resins are carefully selected so that they are of uniform size and colour, and in the manufacture of pale varnishes any dark-coloured resins are carefully picked out. The larger lumps of resin are put through a resin grinding mill or gum crusher to reduce them to lumps of uniform size.

The broken-up gum or mixture of gums is then weighed out and put in a large gum-running pot.

The gum pot in which the gums or resins are melted (or “run,” as it is commonly called in the trade) consists of a large cylindrical copper vessel, which is made in two pieces, the bottom part being riveted on to the body of

the pot with a flange which is wide enough to overlap the furnace bed, and forms a support for the pot, and prevents the flame from going up the sides.

The bottom part of the pot is subjected to very considerable wear owing to being in direct contact with the heat, as well as to the continuous use of stirrers, and requires to be renewed from time to time.

The varnish pots—known as varnish kettles in America—are usually made of copper, but some-

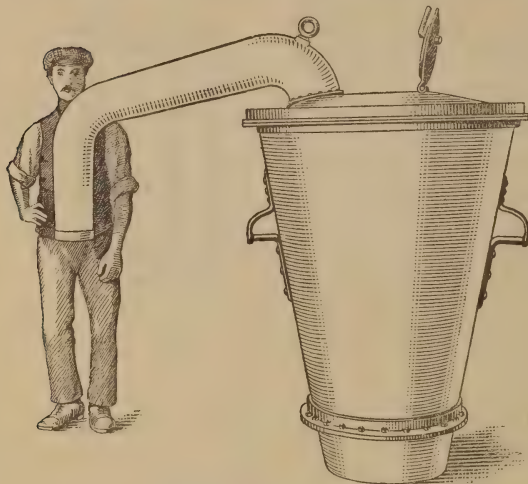


FIG. 37B.—GUM RUNNING POT. DETACHABLE BOTTOM. COVER AND FUME PIPE.

times iron pots are used; and in recent years enamelled iron pots have come into favour, especially in the manufacture of very pale varnishes.

Aluminium varnish pots have been used in the manufacture of varnishes, and are very suitable for the preparation of the very pale varnishes, such as pale copal or French-oil varnishes. On account of their lightness they are very convenient in use, but unfortunately—so far as the author's experience goes—they are not very durable, and the bottoms are apt to fall out after they have been in use for some time. This defect renders them, of course, very dangerous.

Aluminium pots are now often made with flanged-on detachable copper or special bronze bottoms (see Fig. 37). This combined construction affords great strength and resistance, so that burning through becomes practically an impossibility, and the life of the pots is thereby considerably increased.

The size of the pots varies considerably, a convenient size being one that has a capacity of about 100 gallons. Fig. 37A shows the dimensions of a Standard

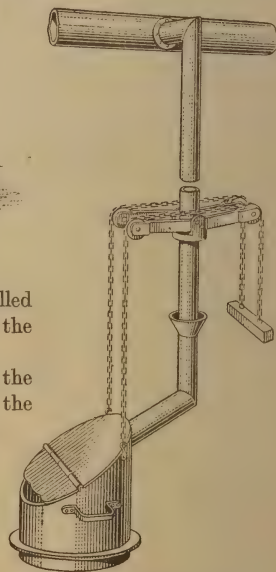


FIG. 38.—VARNISH POT COVER WITH COMPENSATING LIFT.

Aluminium Gum Pot made by the Aluminium Plant and Vessel Co., for "running" 60 lbs. of gum at one operation.

The pots are provided with easily movable covers (Figs. 37B and 38), which can readily be fixed on during the melting operation, and these are connected by means of a pipe with a condensing apparatus where the products of decomposition are collected, particular care being taken that the adjustments are made so that none of the volatile products that are distilled off can run back into the melting-pot.

The varnish pot is placed on, but not attached to, a varnish truck provided with two wheels, and connected with a long handle to the front axle, and provided with an attachment so that the pot may be raised or lowered at will (see Fig. 39).

By means of the iron varnish truck it is a simple matter to move the varnish pots wherever required, and also to raise or lower them to any required height from the bed of the furnace during the melting operation (see Fig. 40).

The top of the furnace is set just below the floor level, and connected with a tall chimney to carry off the products of combustion. The fuel ordinarily used is coke, although gas is sometimes employed.

The varnish pot containing the requisite amount of gum is placed directly over the fire and is supported by its flange on the bed of the furnace. The cover is adjusted and the temperature of the gum is gradually raised to about 340° to 360° C. (650° to 680° F.). Should the temperature rise too quickly, then the heat may be moderated by raising the pot a little above the furnace bed by means of the adjustable attachment fitted to the varnish truck.

As the gum melts large amounts of volatile oils are driven off and are collected in the condensing chambers. When the gum has lost from about 10 to 25 per cent. of its weight—depending on the variety of the gum that is being run—it should be perfectly fluid and limpid and run off the stirrers like a thin oil; further, no particles of hard or melted gum should be detected when the stirrer is gradually worked round the bottom of the pot.

The weight of gum run at a time varies, but as a general rule the charge consists either of 50, 100 or 150 lbs. of gum, though in the manufacture of the paler varnishes it is better to run not more than 50 lbs. at one time.

While the gum is being run, "prepared" linseed oil is being got ready to incorporate with it; and this is usually done by gradually heating up old tanked

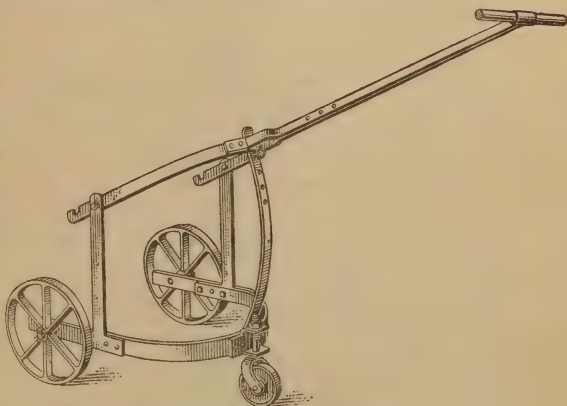


FIG. 39.—VARNISH POT CARRIAGE.

linseed oil—Baltic or refined East Indian oil is the best—to a temperature of 300° F., then stirring in a suitable proportion of red lead, litharge and manganese hydroxide driers, and gradually raising the temperature to about 550° F.

The hot oil thus prepared is added, in small proportions at a time, to the melted resin and vigorously stirred; when the first portion of the oil is in, a sample is put on to a piece of bright tin plate and examined to see if it is perfectly transparent.

The cooled sample on the tin plate must show no signs of white opacity or separation.

If clear and transparent it indicates that complete amalgamation has taken place between the gum and the oil. If the mixture is cloudy then the heating must be continued till a portion taken out is quite bright and transparent. More oil is then added and again tested, and so on till the full amount of oil is added.

The resin and oil mixture is then cooked until the varnish, when spotted on tin, gives a bright transparent product of a thick and sticky consistency. The pot is then run off the fire into the open, and when it has cooled down to about 250° F. it is thinned down to the required viscosity (or "run up") with spirits of turpentine.

The varnish is then pumped while warm through a varnish filter press (Fig. 41), the frames of which are covered with layers of cloth and filter paper. By this means all slimy, gummy

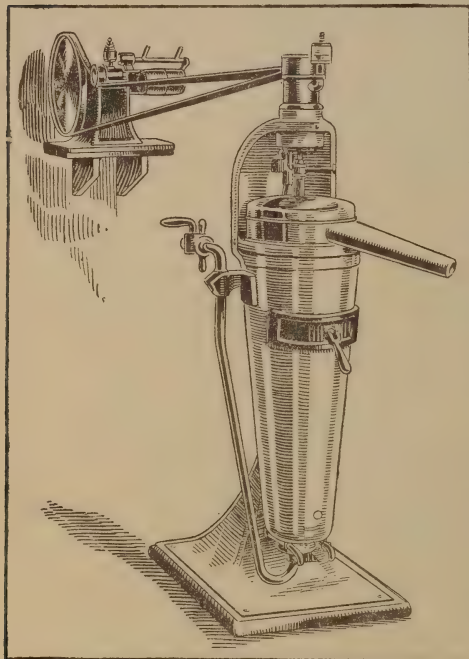


FIG. 42.—SHARPLE'S VARNISH CENTRIFUGE.

matter, mucilage, and suspended impurities are removed, and the clear varnish is then tanked.

Varnishes may also be rapidly clarified by passing them through a centrifuge (see Fig. 42) machine specially designed for this purpose, whereby all the suspended matter is eliminated by means of centrifugal force. The machine operates at a speed of 17,000 revolutions per minute and thus exerts a separating force 16,950 times the force of gravity.

The tank room in which the varnishes are stored is maintained at a temperature of about 80–95° F. in order to clear and age them.

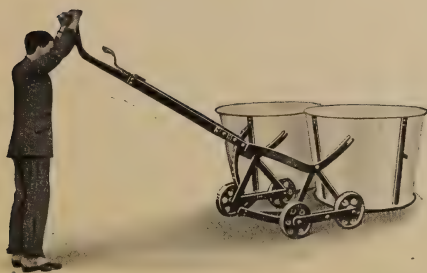


FIG. 40.—VARNISH POT CARRIAGE WITH VARNISH POTS.
(Aluminium Plant & Vessel Co., Ltd.)

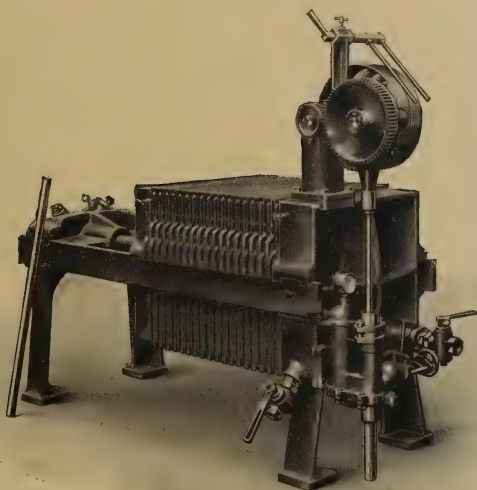


FIG. 41.—VARNISH FILTER PRESS WITH SELF-CONTINUED BELT-DRIVEN PUMP.
(S. H. Johnson.)

Newly-made varnishes are not satisfactory to use, however carefully they may be filtered, as they always contain minute particles of matter in suspension, and dry with a spotty or ridgy film, which is lacking in lustre.

The best class of varnishes are always tanked for about six to eighteen months before use, and sometimes even as long as two years. During the tanking or ageing process the varnishes throw out a sediment, or "foot out" as it is called in the trade, and in process of time this sediment or "foot" gradually settles down to the bottom of the tank, leaving the varnish above bright and clear.

In addition to "footing" out, the varnish, during the ageing process, "bodies" or thickens somewhat, and its drying properties are considerably increased, due partly to the absorption of oxygen from the air.

The well-matured varnish is carefully tested before sending out to see that it has the right viscosity, and that it dries in the right time with a hard, uniform, smooth, glossy, transparent film.

The above description of the plant and the process used in the manufacture of high-grade varnishes is necessarily brief, since the process varies considerably according to the particular grades of varnish that are being made.

Every gum has its own peculiarities as regards its ease of running and the amount of oil with which it will satisfactorily amalgamate; and no definite directions can be given for the preparation of varnishes, inasmuch as these can be learnt only by long experience in the handling of the products.

Sometimes thickened linseed oil—that is, oil which has been heated until it has a high viscosity (commonly known as "stand oil"—see page 225)—is used in addition to linseed oil: blown oils may also be used. The addition of these thickened oils to the melted resin enables the varnish-maker to stiffen up the oil resin mass more readily and to a thicker consistency, and he can therefore use more turpentine in thinning down.

Occasionally oleate or linoleate of alumina is added to prepared linseed oil to help to body it up, and so to produce the required consistency without so much cooking, a process which always tends to darken the finished varnish.

Again, the nature of the driers employed varies enormously; some varnish-makers prefer to use cobalt acetate or linoleate just before thinning out. Others prefer to cook the lead and manganese driers (such as red lead, litharge and manganese dioxide) directly into the oil gum mass at a fairly high temperature in order to produce quickly a thick stringy medium which will readily take a large volume of thinners to reduce it to the right varnish consistency. This method of adding the driers is disadvantageous, as it tends to saponify or soap up the varnish, with the result that the finished product is very dark and lacks lustre; moreover, its wearing properties are apt to be seriously interfered with.

A better method consists in adding the driers in the form of lead manganese resinates or linoleates to the cooked-up mass of gum and oil, and thus prevent any chance of saponification taking place; the varnish thus produced is full of lustre and is pale in colour.

In place of turpentine it is customary in the cheaper varnishes to use white

spirit, or a mixture of turpentine and white spirit, in order to cheapen the cost of production.

The amount of oil required in the manufacture of varnishes varies considerably according to the nature of the resins or "gums" used, and also according to the particular purpose for which the varnish is required.

Varnishes are often classified as "long oil" or "short oil" varnishes, depending on the amount of oil which has been used in their preparation.

Varnishes such as French oil varnishes, carriage varnishes, and body varnishes are "long oil" types, and contain roughly about 20 gallons of oil to every 100 lbs. of gum resin.

They are tough, durable varnishes, and on account of their elastic and hard wearing properties are eminently suitable for outdoor use.

"Short oil" varnishes, on the other hand, are those which contain only a small portion of oil to the gum resin constituent. As a rule they are very hard, but somewhat brittle, and are not suitable for hard wearing outside use. These varnishes comprise those sold under such names as flattening or rubbing varnishes, furniture varnishes, floor varnishes, etc., and also the stoving varnishes.

The amount of oil used in "short oil" varnishes varies from about 8 gallons to 16 gallons for every 100 lbs. of gum used.

The amount of volatile thinners employed in varnishes is about 60 per cent., but this of course varies enormously according to the nature of the varnish and the method by which it is applied. For example, spraying and dipping varnishes are naturally of very low viscosity and contain a very high percentage of volatile thinners.

VARNISH FORMULA

No general formula and methods of working can be given for the preparation of the many varnishes which are usually sold in the trade for the reasons already given, but the recipes given below, taken from Andés, Livache, and other well-known writers on this subject for the preparation of various varnishes which are in common use, will give some indication of the resins and the amount of oils and driers that may be used to produce such products:—

(1) *Finishing Body Varnish.*

Gum Kauri	100 lbs.
Prepared oil	20 gals.
Manganese resinate	4 lbs.
Turpentine	45 gals.

(3) *Hard Church Oak Varnish.*

Congo copal gum	100 lbs.
Boiled linseed oil	22 gals.
Sugar of lead	5 lbs.
Manganese hydrate	2 „
Turpentine	42 gals.

(2) *Hard Carriage Varnish.*

Pontianac resin	100 lbs.
Baltic linseed oil	25 gals.
Litharge	2 lbs.
Red lead	2 „
Manganese dioxide	$\frac{1}{2}$ „
Turpentine	50 gals.

(4) *French Oil Varnish.*

Pale Sierra Leone copal	100 lbs.
Bleached linseed oil	25 gals.
Cobalt acetate or linoleate	$2\frac{1}{2}$ lbs.
Turpentine	50 gals.

(5) *Furniture Varnish.*

Manila gum	100 lbs.
Boiled oil	18 gals.
Stand oil	2 „
Prepared wood oil	2 „
Turpentine or white spirit	42 „

(7) *Japan Gold Size.*

Kauri gum	100 lbs.
Boiled oil	22 gals.
Red lead	5 lbs.
Litharge	5 „
Manganese dioxide	2½ „
Turpentine	45 gals.

Japan gold size is used by sign-writers for lettering purposes with gold leaf, also, when thinned down, as a drier for paints, enamels and varnishes.

Gold size should dry off hard in about two hours, and on account of this always contains a large amount of driers.

It is also used as a medium in the preparation of quick-drying coach colours.

(9) *Cheap Dark Oak Varnish for inside and outside use.*

Manila gum	50 lbs.
Congo copal	50 „
Raw linseed oil	20 gals.
Litharge	5 lbs.
Manganese dioxide	2 „
White spirit	45 gals.

(6) *Flatting Varnish.*

Zanzibar copal	100 lbs.
Baltic oil	15 gals.
Litharge	5 lbs.
Manganese hydrate	2 „
Turpentine	35 gals.

(8) *Shellac Gold Size.*

T.N. shellac	100 lbs.
Prepared oil	30 gals.
Red lead	40 lbs.
Turpentine	100 gals.

(10) *Pale Stoving Varnish.*

Pale kauri gum	100 lbs.
Raw linseed oil	18 gals.
Turpentine	35 „
To stove at 220° F. No drier is necessary.	

ROSIN VARNISHES

Colophony or rosin is largely used in the manufacture of the cheaper grades of varnish, more especially of those varnishes which are intended for indoor use.

As varnishes made from mixtures of rosin and oil do not readily dry off hard, but tend to remain sticky or “tacky,” it is customary to harden the rosin by the addition of lime or zinc oxide.

Rosin may be hardened by dissolving it in white spirit or naphtha, and stirring in zinc oxide or freshly slaked lime till it is all taken up. The usual method is to melt the rosin and add the required amount of lime to it at a temperature of about 300–400° F., stirring well till it is all cooked in, and a portion of the fused mass taken out is perfectly bright and clear when dropped on to glass. The clear fused mass is then thinned down to the right consistency with the necessary amount of turpentine or other suitable solvent.

The lime combines with the rosin forming a calcium resinate whereby the acids of the rosin are neutralised.

The ideal rosin varnish should be neutral, but in practice it is found that if

the neutralisation point is carried too far, the rosin-lime compound is insoluble in white spirit, turpentine, naphtha, etc.

The amount of lime required to completely neutralise rosin (which has an acid value of 180) is roughly 9 per cent. ; but as a rule not more than 5 per cent. of lime is used, whereby the acid value of the rosin is reduced to about 18.

Rosin varnishes made by dissolving calcium rosinate or "hardened" rosin in turpentine or white spirit dry very quickly, and with a high lustre ; and as they are very cheap they are largely used as varnishes for indoor work and for making cheap varnish paints.

As these varnishes are very brittle it is usual to add a proportion of boiled linseed oil to toughen them, but only a limited amount of oil can be used, otherwise such varnishes will not dry off hard enough to be satisfactory for general use.

WOOD OIL VARNISHES

In recent years large quantities of varnish suitable for both inside and outside use have been made by the addition of wood oil or tung oil to rosin or rosin esters.

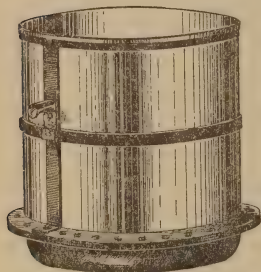


FIG. 43.—STANDARD 130-GALLON ALUMINIUM OIL BOILING POT WITH FLANGED-ON COPPER OR SPECIAL BRONZE BOTTOM.

Rosin ester gum is the neutral product obtained by the complete esterification of the abietic acid of common rosin or colophony. It is not a pure chemical compound, as in addition to abietic acid rosin contains varying amounts of neutral unsaponifiable hydrocarbons, the proportions depending on the origin and method of manufacture of the rosin.

Rosin ester gums are glycerides, and are manufactured by combining rosin with glycerine (see page 163), whereby the acid value of the rosin is reduced to about 10.

Ester gum varnishes are prepared in the following way :—Hankow wood oil is heated up as rapidly as possible to 220° C. (428° F.) in a copper, aluminium, or iron pot (see Fig. 43) ; 2 per cent. of litharge is then stirred in until completely dissolved, the temperature being allowed to rise to 260° C. (500° F.). The pot is then removed from the fire and allowed to cool down. The oil rapidly thickens up, and if allowed to go on cooling would solidify or form a jelly-like mass (polymerise). At this stage 25 per cent. or more rosin ester gum is added and stirred well in. The ester gum melts and completely amalgamates with the wood oil, and if a sample be taken out and dropped on to glass it gives a tough, bright, transparent hard mass.

When the contents of the pot have cooled to about 160° C. (320° F.) about $\frac{1}{2}$ or $\frac{1}{4}$ per cent. of cobalt acetate or linoleate should be stirred in, after which turpentine or white spirit is added.

Part of the wood oil may be replaced by stand oil if it is found that this varnish dries too rapidly or skins on the top after standing.

These varnishes on account of their low acidity possess the advantage of not thickening up or "livering" when mixed with either white lead, zinc oxide, or other pigments, and hence may be used as mixing varnishes.

Wood oil ester gum varnishes are exceedingly durable and are eminently suitable for both indoor and outdoor use. Moreover, by reason of their excellent waterproof qualities, due to their wood oil content, they have been largely used as boat or yacht varnishes (spar varnishes).

Wood oil varnishes are largely used on account of their great elasticity as the most suitable oil varnish for protecting doped fabric.

SPECIFICATION FOR VARNISHES

As there are so many different qualities of varnish manufactured, no general specification is of much use unless the particular purpose for which the varnishes are going to be used is known.

The chief qualities required in a high-class varnish may nevertheless be enumerated briefly as follows:—

The varnish should be bright and transparent, and free from any suspended matter, and when kept in a suitable container in a warm room for three months should not throw out any sediment or "foot." This shows that the constituent parts are well amalgamated, and that the varnish has been tanked a sufficient time for it to age or mature properly.

The paler varnishes are to be preferred to the dark ones provided that they dry off hard and without any tack within the required time.

The varnish on drying off should give films of high brilliancy and lustre and not show any signs of blooming on exposure.

The surface of the varnish should be perfectly smooth, free from picks or bits, and show no indication of ridging, crinkling or pin-holing.

Outside varnishes should be tough and elastic, and on exposure to the weather should not crack or lose their lustre ("face") after twelve months.

Flatting or "rubbing" varnishes after drying off hard should rub down with pumice to produce a dull surface and not show any signs of sweating.

Sweating in a flatting varnish indicates that too much oil has been used in its preparation. A flatting varnish is used as an undercoating varnish, and a finishing varnish will only adhere or "key on" if the under surface is perfectly flat or "matt." A varnish if applied to a glossy surface does not adhere firmly, and on drying tends to "crawl" and become crinkly or, as it is commonly called "sisses."

The viscosity of the varnish should be determined in a suitable viscometer (Ostwald, Fig. 44) in order to see that it is equal to the standard required and that the right amount of volatile thinners has been used.

LITHOGRAPHIC VARNISH, STAND OIL

Lithographic varnish (litho or stand oil) is used in lithographic printing, in the manufacture of printers' inks, and also in the manufacture of paints and enamels.

Stand oil is derived from the German word *Standöle*, because on standing the mucilage coagulates and separates out from these oils.

Lithographic varnish is made by heating old clarified tanked oil in a large iron pan set in brickwork and provided with a hood to carry off the pungent acrid fumes which are formed. The furnace below the pot is bricked off, to secure that if, by any chance, the oil should boil over it cannot come into contact with the flames; this affords a good protection against fire. The oil is gradually heated up to 250° F. and held at this temperature till all frothing has ceased, *i.e.* till all the moisture has been driven off. The oil is then slowly raised to 570° F., and thence to 610–620° F. This heat must be kept up until the oil has been brought to the right consistency. Any tendency to rise or boil over must be counteracted by adding a little cold oil. The time required to thicken up the oil varies from about two hours heating to ten hours, according to the strength or thickness of the finished product.

Lithographic varnish is also made by heating up linseed oil to its ignition point in large movable iron pans. The pans are then withdrawn from the fire and the issuing vapours ignited by means of a lighted taper. The oil burns with a pale blue flame, which gradually becomes luminous and smoky. At this stage the fire is put out by placing a large piece of sheet iron over the pot and thus excluding all the air.

The pot is again put on to the fire and heated up, and the igniting process repeated, and so on till samples taken out and cooled down indicate that the oil has reached the desired consistency. Litho varnishes are manufactured in the following consistencies:—Tint, thin, middle, strong, and extra strong.

Stand oils are usually sold for use in paints and enamels, and are of a medium consistence. They sometimes contain a small proportion of driers, when they are known as drying stand oils.

They should be pale in colour, and must not be sticky, and should dry with a good gloss.

When linseed oil is heated it gradually thickens, and its gravity increases, while the iodine value falls. This thickening of linseed oil on heating is due to polymerisation.

The following figures obtained by the author on heating linseed oil on the large scale for the manufacture of stand oil will indicate the changes taking place during this process:—

Time of Heating. Hours.		Gravity at 15·5° C.	Free Oleic Acid.	Saponifica- tion Value.	Iodine Value.
0	Linseed oil	0·9320	2·5	191·5	184·0
2	Extra thin stand oil	0·9452	3·19	186·5	157·0
3	Thin stand oil	0·9465	3·85	178·4	123·2
4	Medium stand oil	0·9574	4·43	183·8	115·4
5	Stout stand oil	0·9650	5·34	185·0	111·5

ANALYSIS OF OIL VARNISHES

The complete analysis of oil varnishes, by which we mean the identification and estimation of the amount of the particular gum resins, and also the oils which have been used in their preparation, is, in the present state of our knowledge, quite impossible, in spite of many statements to the contrary.

This can easily be realised when one considers that varnishes are very often made up from mixtures of two or more gum resins in conjunction with linseed oil, or mixtures of linseed oil, wood oil and stand oil, and that during the process of fusion and amalgamation they undergo very considerable changes, being both oxidised and polymerised, so that even if processes could be devised whereby the ingredients could be separated from one another the products thus obtained would show little if any of the characteristics of those originally used.

Fortunately, however, the complete analysis of a varnish in this sense is not required, and all that is necessary is to be able to evolve a scheme whereby such products may be classified and duplicated.

The usual procedure in the examination of a varnish of unknown composition is to subject it to a series of physical and chemical tests and to compare the results with similar tests on varnishes of known composition; by this means much valuable information may be obtained by anyone familiar with the different gums used, and the various and intricate details of varnish manufacture.

In this way no difficulty will be found in matching a varnish with one which, although it may not contain identically the same constituents (gums, oils, etc.), will nevertheless be its equal for all practical purposes.

(1) *General Appearance*

The sample of varnish under test is placed in a standard varnish tube and its colour and "run up" or viscosity compared with that of other standard varnishes placed in identically similar tubes. The viscosity may, if required, also be determined accurately in an Ostwald viscometer (Fig. 44).

Simple form of Ostwald Viscometer.—This apparatus consists essentially of two glass tubes of different diameters joined together at one end, while the narrower tube has a bulb blown near the free end. A mark "A" is made on the glass a little above the bulb, and a second, "B," is made some distance below the bulb. Excepting where very viscous liquids are under examination, it is desirable that the tube from the lower end of the bulb to just below the mark "B" should consist of capillary tubing.

To use the apparatus it should be kept in a thermostat, and a convenient amount of the varnish should be introduced through the wider tube by means of a mouthpiece attached to the top of the narrower tube; varnish is drawn up into this arm until

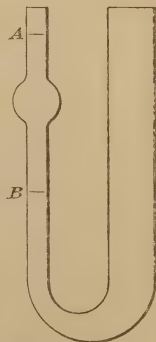


FIG. 44.—OSTWALD VISCOMETER.

its level is above the mark A. The varnish is then allowed to fall in the tube under the action of gravity, the time taken for the surface to fall from A to B being carefully observed with a stop watch. This interval is then compared with that obtained for a standard varnish of known viscosity under the same conditions in the same viscometer.

The smell of the varnish will give a good general idea as to its value. A pleasant gummy, aromatic, turpentine odour indicates a high-class varnish, which has been made up from gum resins and thinned down with turpentine; whereas varnishes which contain large amounts of rosin, or rosin and wood oil, and petroleum thinners possess a peculiar smell, readily identifiable by anyone who is at all familiar with these products.

If the varnish be at all turbid or cloudy it is an indication either that the driers have not been properly incorporated during the process of manufacture, or that the varnish has not been tanked long enough. Very often a varnish may cloud or "throw out" if brought from a warm room and left for some time in the cold. Turbid or cloudy oil varnishes always give unsatisfactory results, and only bright and clear varnishes should be used.

The viscosity of a varnish varies considerably according to the nature of the varnish and its method of application.

Finishing varnishes, such as body and carriage varnishes, which are to be applied by a brush, should be of stout consistency or body so that good flowing coats may be applied, which will dry off with a high lustre. Undercoating varnishes, flattening varnishes, etc., are as a general rule of a much thinner consistency, as they are required to dry off quickly with hard surfaces and are not required to have any particularly high gloss. Gold size and rosin varnishes are usually low in viscosity.

(2) *Working Properties*

The working and flowing properties of a varnish will give valuable indications of its quality. A high-class varnish will brush out easily without any pull and flow evenly over the surface to which it is applied. Cheap varnishes containing rosin are difficult to work and "lay off" and soon begin to pull on the brush. Some varnishes show an objectionable tendency to froth or bubble when worked under the brush, due to the high volatility of the solvent used in thinning them down.

(3) *Time of Drying*

The time of drying of a varnish should always be carefully noted, as this gives an excellent indication of the nature of the varnish under examination. The time of drying varies considerably, *e.g.* a high-class elastic finishing body varnish will require, at ordinary room temperature, about twelve to fourteen hours to dry off hard, while a gold size, on the other hand, should dry off in about one to two hours. This test is usually carried out by flowing the varnish on to a glass strip and placing it in a vertical position; the times which the varnish takes to become "tacky," "surface dry," "dry" and "hard dry" are then noted.

Varnishes containing untreated wood oil, or wood oil that has not been properly polymerised, show a tendency to "web" or "crocodile skin" when the film on glass is allowed to dry in a cupboard exposed to the fumes from a coal gas flame.

A sample of the varnish should also be brushed on to a prepared board, and the time of drying noted in this case also, so as to check the results obtained on the glass strips.

(4) *Nature and Characteristics of the Dry Film*

An examination of the dried varnish films when perfectly hard is of great value in estimating their toughness and elasticity. The tougher and more elastic the films are, the greater the durability and weather resisting properties of the varnish.

A varnish which yields hard yet brittle films, such as is the case with rosin varnishes, wear badly on exposure to the weather; this is due to the action of the rain and moisture and variations in temperature causing contraction and expansion, whereby the films crack and perish in a very short time.

The toughness of a varnish may be judged by taking the dried film on glass and scratching it with the thumb nail or with a sharp instrument such as a knife blade.

The brittle varnishes will powder up and dust off readily, while the tough varnishes may be scraped off in the form of tiny ribbons.

In these tests care must be taken to see that the varnish film is perfectly hard and dry throughout, otherwise the test will not be accurate.

A good plan is to test the film of varnish at intervals of time extending over a couple of months or more, so as to get absolutely reliable information, since not infrequently varnishes which are moderately tough after two or three days drying become very brittle after keeping for some time.

Another method consists in varnishing a piece of thin tin plate and, after the varnish is thoroughly dry, bending the tin and noting the condition of the varnish after it has been subjected to this strain.

The hardness of a varnish may be tested and a numerical value given to it by an instrument devised by A. P. Laurie and F. G. Baily.

An apparatus described by H. Wolff¹ consists of a triangle formed by three wooden strips, the base of which is hinged to the face of a base board. At the apex of the triangle is fitted a blunt knife edge directed towards the face of the base board. Pressure is exerted on the knife edge by means of a small loaded dish set on the apex directly over the knife edge, and so arranged as to be counterpoised to zero load by a lever carrying a sliding weight, and set at right angles into the hinged base of the triangle in a direction away from the apex.

The varnish test plate is fixed to the two strips which slide in guide rails fastened to the base board, and is moved at a definite rate so that the film comes in contact with the knife edge.

By means of a paper scale attached to the test piece a number of "cuts" can be made at varying loads and compared.

By substituting a strip of tinned iron in place of the knife edge and taking

¹ *Farben Zeitung*, August 1922 (O.C.T.J., 1922).

observations at loads slightly above zero the progress of drying of a varnished surface may be noted by the adhesion or otherwise of the testing edge.

The dry film of varnish on wood should also be tested by rubbing down with sandpaper and noticing how it works under such treatment.

Only flattening varnishes which are "short oil" varnishes will rub down in a satisfactory manner, giving perfectly flat surfaces, which do not sweat, and to which a subsequent coat of finishing varnish will adhere firmly.

(5) *Weathering and Waterproof Properties*

The weathering tests on a varnish should be carried out in the following manner:—Prepared boards varnished with one and two coats of the varnish under test are hung up outside in an exposed position and examined from time to time.

Cheap rosin varnishes will spot in a few days, and after a few weeks will crack all over. On the other hand, outside varnishes, such as elastic oak varnish, etc., will keep their gloss or "face" and show little signs of wear even after twelve months' exposure.

Varnishes which contain an excess of driers are found to wear badly on exposure, as such excess plays a very active part in favouring speedy "super-oxidation," whereby the film is rapidly corroded and perishes.

As such exposure tests take time, and very often it is desirable to form some estimation of the wearing properties of a varnish in a few days, the author has found that fairly good results may be obtained as to the durability or wearing properties of a varnish by immersing the dried films in a dilute solution of sulphurous acid, then allowing to dry out in the open air.

The waterproof qualities of a varnish are best determined by immersing varnished strips of tin in a bowl of water for twelve hours, then removing and allowing to dry in the open. The varnishes which contain much rosin remain more or less permanently white, and this also applies to some of the softer gum varnishes.

Dammar varnishes, and varnishes made up of wood oil and a small proportion of ester gums, are remarkably waterproof and on exposure to water are little affected; if subsequently dried they again become bright and clear, without showing any signs of corrosion.

A simple test, which is very often carried out by coach-painters, consists in placing a wet sponge on their varnished work after it is thoroughly dry, and leaving over night. Next morning the varnish should show no change of colour, and if gently rubbed with a soft cloth should polish up bright and dry and leave no trace of the application of the sponge.

ANALYTICAL EXAMINATION

The methods in general use for the analytical examination of varnishes are briefly as follows:—

The specific gravity, viscosity and acid values are first determined in the usual manner.

Driers

The next procedure consists in ashing 5 or 10 gms. of the varnish, weighing the ash, and estimating the percentage of metallic driers present by following the method given on page 248; or, alternatively, the driers may be extracted by agitation with hydrochloric acid.

Volatile Matter

The volatile matter is determined by weighing out 100 gms. of the varnish into a flask connected with a condenser. The varnish is heated in an oil bath gradually to about 130° C., and a current of steam is pressed through till all the volatile matter is driven off. A rough determination may be quickly made by heating 10 gms. of the varnish on a sand bath till no more volatile matter is driven off, but owing to the high temperature necessary to drive off all the volatile constituents of the varnish, decomposition is liable to take place, and this would cause the result obtained to be too low.

The residue obtained gives the amount of oil and resin present in the varnish.

Separation of Oil and Resin

The separation of the oil and resin constituents of a varnish is carried out by first saponifying the residue obtained (after the removal of the volatile constituent), by boiling with alcoholic potash under a reflux condenser until as complete saponification as possible has taken place. The unsaponifiable matter is extracted with ether in the usual way, and the resin oil soap solutions are acidified with hydrochloric acid and taken up with ether. The ether is removed by distillation, the fatty acids and gums dissolved in absolute alcohol and esterified by passing in dry hydrochloric acid until saturated (Twitchell's method).

In this way the fatty acid esters are separated from the resin acids and the total amount of resins present in the varnish estimated.

CHAPTER XIX

THE MANUFACTURE OF SPIRIT VARNISHES, CELLULOID VARNISHES, LACQUERS AND DOPES

SPIRIT varnishes are made by dissolving resins in oil of turpentine, alcohol, acetone, and other volatile solvents without the addition of any drying oils. These varnishes, as a rule, dry off very quickly, with a high lustre, and hence are largely used as protective coatings for indoor work where quick results are required.

The manufacture of spirit varnishes is an extremely simple operation, and is carried out usually by dissolving the resins in the cold in the various selected solvents in the following manner:—

The broken-up resin is emptied into a large barrel, which is fixed on to supports on which it can revolve (Fig. 45). The required amount of solvents is added, the cover screwed on, and the contents churned for a few hours till solution has taken place.

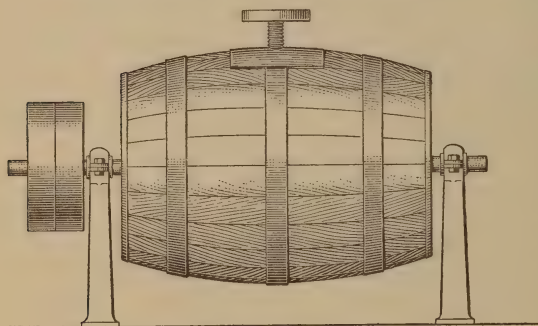


FIG. 45.—SPIRIT VARNISH CHURN.

In the case of the higher boiling paint solvents it is usual to melt up the resins in a steam pan or by direct heat over a fire, and then to stir in the solvent; or, alternatively, to warm up the solvent and stir in the finely-powdered resins.

By this means the process of dissolving the resins is very considerably accelerated. The varnishes may be filter pressed to remove any suspended matter.

ALCOHOLIC SPIRIT VARNISHES

The most important of the alcoholic spirit varnishes, and the one in most general use, is shellac varnish, which is manufactured in large quantities for use in the polishing of furniture, and is sold under the name of French Polish.

French polish is made by dissolving shellac in methylated spirit in the cold

in the following manner :—5 lbs. of Venice turpentine and 60 lbs. of orange shellac are churned for six hours with 40 gallons of methylated spirits. The resulting varnish has an orange-brown turbid appearance, and dries in about ten minutes, with a hard lustrous coat. The Venice turpentine helps to toughen the film and so increase its durability.

This varnish is applied with a rubber; a large number of exceedingly thin coats are laid on to the article which is being polished, and by this means a beautiful lustrous finish is obtained.

For white varnishes bleached shellac is used; for dark varnishes ruby or garnet shellac.

Knotting varnishes, which are so largely used by painters as a first coat or priming on wood, are also prepared by dissolving shellac in methylated spirits.

In place of ethyl alcohol some manufacturers use methyl alcohol, more especially in America; but on account of its toxic qualities its use is not to be recommended.

WHITE HARD SPIRIT VARNISHES

These varnishes are made by dissolving spirit soluble Manila gums in alcohol or methylated spirits, usually about 3 lbs. of Manila gum to 1 gallon of alcohol being the proportion adopted. They are clear, transparent varnishes and are largely used as paper varnishes.

For making spirit Manila varnishes only those copal gums should be selected which will readily dissolve to a clear solution, free from slimy or stringy qualities. They dry off very quickly with a high lustre.

BROWN HARD SPIRIT VARNISH

This varnish is made in a similar manner to white hard spirit varnish, but a small percentage of Bismarck brown is added to give the requisite colour.

ROSIN ALCOHOLIC SPIRIT VARNISHES

These are made by dissolving pale rosin in alcohol, about 4 lbs. of rosin to 1 gallon of alcohol. They are rather brittle, hence are only used for common work.

In addition to the resins already mentioned, many others can also be used in alcoholic solution for the preparation of quick-drying lustrous varnishes, among which may be mentioned gum mastic, sandarac, elemi, etc.

Various softening agents may be used in small proportions in conjunction with the above-mentioned resins in order to toughen their films and prevent them from flaking off. The usual ones employed are castor oil, Venice turpentine, gum thus, copaiba balsam, and Burgundy pitch.

The following recipes taken from Livache, Bottler, Hurst, and others will give a general indication of the various proportions which are commonly employed in the preparation of alcoholic spirit varnishes, and the purposes for which they are used :—

(1) *Dark Brown Polish.*

Garnet shellac . . .	40 lbs.
Methylated spirit . . .	25 gals.

(2) *White Polish.*

Bleached shellac . . .	40 lbs.
Methylated spirit . . .	27 gals.

(3) *Shellac Spirit Varnish.*

Orange shellac . . .	10 lbs.
Venice turpentine . . .	3 „
Alcohol	36 gals.

(4) *Bookbinders' Varnish.*

Shellac	82½ lbs.
Spirits of turpentine . . .	3 gals.
Methylated spirit . . .	80 „

(5) *Paper Varnish.*

Sandarac	50 lbs.
Thick turpentine . . .	30 „
Alcohol	15 gals.

(6) *Rosin Varnish.*

Pale rosin	23 lbs.
Venice turpentine . . .	4 „
Alcohol	16 „

(7) *Paper Varnish.*

Manila copal	16 parts
Venice turpentine . . .	5 „
Alcohol, 95 per cent. . . .	30 „

(8) *Bookbinders' White Varnish.*

Sandarac	6 parts
Mastic	3 „
Elemi	3 „
Alcohol	150 „

(9) *Negative Varnish for Photographers.*

Gum sandarac	5 ozs.
Gum benzoin	2 „
Methylated spirit	½ gal.

COLOURED LACQUERS

Coloured lacquers are made in large quantities for colouring metals, wood, leather goods, etc. They are applied to metals in two ways, known as “cold lacquering” and “hot lacquering.”

The colouring of the lacquers or spirit varnishes is usually effected by adding to them concentrated alcoholic solutions of aniline dye-stuffs. Formerly the naturally occurring colouring substances such as dragon's blood, turmeric, gamboge, logwood extract, and others were used for this purpose, but at the present time these have been replaced by spirit aniline colours. These colours are soluble in alcohol, and are manufactured in all tones and shades suitable for different types of work. The following recipes for the preparation of various coloured lacquers will give a general idea as to their composition:—

(1) *Deep Gold Lacquer.*

Bleached shellac	3 lbs.
Methylated spirit	2 gals.
Concentrated solution of Dia-	
mond-Fuchsine	¼ pint

(2) *Pale Gold Lacquer.*

Bleached shellac	10 ozs.
Methylated spirit	1 gal.
Aniline yellow concentrated	
solution	¼ pint

(3) <i>Blue Lacquer.</i>		(4) <i>Violet Lacquer.</i>	
Shellac	5 ozs.	Shellac	2 ozs.
Sandarac	5 „	Sandarac	8 „
Elemi	2 „	Elemi	3 „
Alkali blue concentrated solu- tion	$\frac{1}{2}$ pint	Methylated spirit	1 gal.
Methylated spirit	1 gal.	Methyl violet (concentrated alcoholic solution)	$\frac{1}{4}$ pint

Spirit Varnish Stains are largely used for the staining of wooden floors, etc. They are made by adding Vandyke brown, Bismarck brown, and other colouring matters to shellac, Manila and rosin spirit varnishes.

TURPENTINE SPIRIT VARNISHES

These spirit varnishes may be made by dissolving the resins in the turpentine (or turpentine substitutes such as white spirit, benzol, etc.) in the cold in precisely the same way as described under the alcoholic spirit varnishes.

In general, however, it is customary to melt up the resins and stir in the volatile solutions, as by this means much quicker solutions are obtained. Turpentine varnishes dry more slowly than alcohol varnishes, hence are more easy to apply.

DAMMAR VARNISH

This varnish is largely used as a paper varnish under the name of crystal paper varnish. It is also used in the preparation of white enamels, as, on account of its low acidity, it can be mixed with zinc oxide without any "livering" or thickening up taking place. The enamels thus prepared are of a pure white colour and dry quickly with a high gloss.

Dammar varnish is prepared by melting pale dammar gum and thinning down to the right consistency with turpentine or white spirit. The following proportions may be used :—

Dammar	10	ozs.
Sandarac	5	„
Mastic	1	„
Turpentine	20	„

The mastic and sandarac gums are added to give toughness and elasticity to the varnish.

ROSIN, TURPENTINE SPIRIT VARNISHES

These varnishes may be prepared by churning rosin or hardened rosin with turpentine till solution is effected, or the rosin may be melted and the turpentine stirred in till the required consistency is obtained.

White spirit and naphtha are often used in place of turpentine to cheapen the varnish.

Rosin spirit varnishes are largely used as furniture varnishes and cheap oak

varnishes for inside work. They dry with brilliant glossy surfaces, but are too brittle to be very serviceable, and are liable to powder off on rubbing.

They are also used in the manufacture of common quick-drying varnish paints with the addition of pigments such as red oxide, lithopone, carbon black, and so on.

The Analysis of Spirit Varnishes

The analysis of spirit varnishes is very much easier matter than that of an oil varnish. The volatile matter is estimated by evaporating about 5 gms. of the sample in a steam oven till constant in weight. The residue is then tested for rosin by the Liebermann-Storch reaction (see page 162).

A small portion of the residue is next ignited, when, if shellac be present, it will be readily detected by the characteristic odour which it gives off on burning.

The determination of the iodine value of the residue will give approximately the proportion of shellac present in a mixture of rosin-shellac varnish. In calculating the results the iodine value (Wijs) of shellac is taken as 18 and that of rosin as 228.

In the case of dammar varnishes the amount of rosin present may be ascertained by determining the acid value, taking the acid value of dammar as 20 and that of rosin as 180.

The nature of the volatile solvents may be accurately determined by distilling about 100 gms. of the varnish and examining the distillate in the usual manner.

CELLULOID AND NITROCELLULOSE VARNISHES

When cellulose (cotton wool, cotton waste, etc.) is treated with a mixture of nitric and sulphuric acids, it is converted into pyroxyline or gun cotton— $C_{12}H_{14}(NO_2)_6O_{10}$, or into dinitrocellulose.

Nitrocellulose is converted into celluloid by mixing it with camphor and heating under pressure. Both gun cotton and celluloid are largely used at the present time in the manufacture of varnishes and lacquers.

These varnishes are made by churning nitrocellulose or celluloid with amyl acetate or butyl acetate to a syrupy consistency, then thinning down to the required consistency with a mixture of equal parts of alcohol and benzol. In place of alcohol and benzol other solvents may be used such as ether, acetone, etc.

Nitrocellulose and celluloid varnishes are perfectly clear, colourless varnishes, and are very volatile and highly inflammable. They are extensively used as transparent lacquers for metal work, etc.; for decorative work they may be coloured with various aniline dye-stuffs soluble in the lacquer.

Various pigments such as zinc oxide, carbon black, iron oxide, etc., ground in castor oil and thinned down with these varnishes are now in general use as protective coatings for metal work, doped aeroplane fabric, and so on. They are usually applied by spraying, and dry off rapidly, giving beautiful, tough, hard films. In recent years they have come rapidly into favour on account of their many valuable

properties, and have for many purposes replaced stoving and air-drying varnishes and enamels.

Softening agents such as castor oil, dammar gum, Canada balsam, and other soft resins are usually added to these lacquers and enamels to toughen them, and at the same time to enable them to "key on" more readily to the surfaces to which they are applied.

Nitrocellulose varnishes are also sold under the name of collodion and zapon varnishes.

DOPE

Cellulose acetate varnishes, commonly known as "dope," are used for rendering the fabric on aeroplane wings taut. They are brushed on to the fabric *in situ*, one coat being laid on the other. About four coats of varnish are usually necessary in order to obtain the desired tautening effect.

Cellulose acetate, prepared by treating cellulose with acetic anhydride, is a soft white fibrous material which, unlike gun cotton, has the merit of being non-flammable.

The varnish is prepared by stirring the cellulose acetate into a mixture of acetone (or calcitone, methyl ethyl ketone), benzol, and alcohol, sufficient solvent being used to give the desired viscosity. A small proportion of softening agents such as benzyl alcohol, triacetin, triphenylphosphate, etc., are added in order to toughen the films given by the varnish on evaporation.

Formerly tetrachlorethane was used as a solvent for cellulose acetate in the manufacture of dope, but owing to its toxic properties its use was abandoned.

Dope is a clear, transparent varnish which when poured on to glass quickly evaporates, giving perfectly clear, tough, transparent films, which may be readily removed from the glass. The presence of excess of moisture, or unsuitable softening agents, will cause the films to dry off white and be brittle, in which case the varnish should be condemned.

Owing to its poor weather-resisting properties it is usual to protect the doped fabric with pigmented cellulose nitrate varnishes, those of a reddish or khaki colour affording greater protection than those coloured with white or light tints.

Pigmented Dope

This is prepared by adding a small percentage of pigments (usually of a reddish or khaki colour) finely ground in a medium of triacetin or benzyl alcohol to the cellulose acetate varnishes. It is used in place of ordinary clear dope on account of its greater durability and wearing qualities, and thus avoiding the necessity of applying a pigmented protective coating over them.

Dopes made on a nitrocellulose basis, and to which certain materials have been added to render them non-inflammable, are also used in place of cellulose acetate dopes. They are considered to be fully equal if not superior to dopes made from cellulose acetate as regards durability and tautening properties.

CHINESE AND JAPANESE LACQUER

Natural lacquers are obtained from various species of trees, both native and cultivated, which grow in China, Japan, India, Ceylon and Burma.

Chinese and Japanese lacquer is the liquid sap of the *Rhus vernicifera* D.C., a species of the lac tree, which is grown extensively in Japan. The liquid sap known as "kiurushi" exudes on making cuts on the trees in the form of a thick, creamy, light-coloured fluid, of a specific gravity of 1.002, which rapidly darkens on exposure.

It contains from 64 to 85 per cent. of urushic acid ($C_{14}H_{18}O_2$) and 9 to 26 per cent. of water, 3 to 6 per cent. of gum arabic, together with a little oil and albuminous matter.

These natural lacquers possess the remarkable property of drying more rapidly in a damp atmosphere than in a dry one, owing to a fermentation process which takes place whereby the urushic acid becomes oxidised to oxy-urushic acid $C_{14}H_{18}O_3$. This varnish has been used by the Chinese and Japanese from a very remote period (according to Quinn from 500 to 600 B.C.) for the lacquering of their wares.

The results obtained by the Japanese with these natural lacquers is truly remarkable, excelling all other varnish work as regards the beauty and lustre of the finish obtained.

CHAPTER XX

DRIERS OR SICCATIVES

As the drying oils which are used in the manufacture of paints and varnishes set, at ordinary temperatures, far too slowly for the purpose for which they are usually intended, it is necessary to add to them certain metals or their compounds in order to accelerate this drying or setting process. Such additions are known as driers or siccatives, and by their aid paints and varnishes which in the ordinary way would take two or more days to dry can be made to dry in a few hours.

According to Fokin the following metals or their compounds assist the oxidation or drying property of linseed oil in the following order, arranged according to their activity :—Cobalt, manganese, chromium, nickel (iron, platinum palladium), lead, calcium, barium, bismuth, mercury, uranium, copper, zinc.

He also shows that the rapidity of the reaction varies in proportion to the cube root of the concentration of the drier.

According to Hartley, Mulder and others, the function of the drier is to act as a catalyser or an oxygen carrier, taking up oxygen from the air and transferring it to the oil, and in so doing undergo alternately the opposite processes of oxidation and reduction. In support of this theory it is noteworthy that the metals which are the most effective as catalysers are those which readily form higher and lower oxides.

The above-mentioned metals (in an extremely fine state or sub-division) may be used as driers, but in practice it is found more convenient and efficacious to use oxides and salts—especially certain organic salts—of these metals.

The principal substances used commercially as driers are the oxides or salts of lead, manganese, and cobalt as follows :—

LEAD DRIERS

Litharge (PbO).

Red Lead (Pb_3O_4).

Lead Acetate or Sugar of Lead ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$).

Lead Resinate.

Lead Linoleate.

Lead Tungate.

MANGANESE DRIERS

Manganese Dioxide, Black Oxide of Manganese (MnO_2).

Manganese Hydroxide, Umber ($\text{Mn}(\text{OH})_2$).

Manganese Borate (MnB_2O_4).

Manganese Acetate ($\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$).

Manganese Chloride (MnCl_2), $4\text{H}_2\text{O}$.

Manganese Sulphate (MnSO_4), $5\text{H}_2\text{O}$.

Manganese Resinate.

Manganese Linoleate.

Manganese Tungate.

COBALT DRIERS

Cobalt Acetate.

Cobalt Linoleate.

Cobalt Resinate.

Recently oxides and salts of vanadium have been used as driers, and it is claimed that these bodies act most vigorously as catalysers even when present in very minute proportions. It is doubtful, however, if they will come into general use, as, comparatively, their cost is high and they tend to darken the oils in which they are dissolved.

Zinc oxide and zinc sulphate are also occasionally used as driers—usually in conjunction with lead or manganese; but as their drying properties are extremely small their value as driers is problematical.

LEAD DRIERS

LITHARGE (PbO)

Litharge or lead monoxide is obtained when metallic lead is oxidised at high temperatures. It comes on to the market in the following forms:—

Canary Litharge.—A pale yellowish coloured powder, with an extremely fine and soft texture.

Ordinary Litharge.—A reddish yellow powder; and

Flake Litharge, a coarse glistening flaky powder of a reddish colour.

All three forms of litharge may be used as driers, and on heating with linseed oil readily dissolve, forming a drying oil, which will dry at ordinary room temperatures in about eight to twelve hours.

The amount of lead required to make an oil or varnish dry in a reasonable time is comparatively small, 0.5 to 2 per cent. being about the usual proportion necessary, except in those cases, such as in the manufacture of gold size (see page 223), where the material is required to dry off in an hour or two, when much larger quantities are necessary.

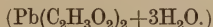
The chief impurities in litharge are metallic lead, lead sulphate and red lead, all three usually being classed together as insoluble matter.

The purity of a litharge may be ascertained by boiling 5 gms. with dilute acetic acid, filtering in a Gooch crucible, washing well with hot water, drying and weighing. The insoluble matter should not exceed 0.5 per cent.

RED LEAD

See Chapter X., page 114.

LEAD ACETATE (NEUTRAL) OR SUGAR OF LEAD



Lead acetate or white sugar of lead is manufactured by dissolving lead or litharge in acetic acid and crystallising out. To obtain it in its finest form it is necessary to recrystallise.

It crystallises in transparent colourless rhomboidal prisms, which whiten on exposure to the air. It has a sweet unpleasant metallic taste, and smells slightly of acetic acid.

It dissolves readily in ordinary water, giving as a rule a white turbid solution, which may be cleared by the addition of a few drops of acetic acid. The turbidity is due to the lime present in the ordinary tap water, which precipitates finely divided white lead hydrate, which again dissolves to a clear solution on the addition of acetic acid.

Crystallised lead acetate melts at 75° C. ; at higher temperatures it decomposes into lead carbonate and acetone. It is slightly soluble in alcohol.

BASIC SUGAR OF LEAD

Sugar of lead has the property of dissolving considerable quantities of litharge forming basic salts. Thus when one equivalent of neutral acetate of lead solution is boiled with one or two equivalents of litharge we get formed respectively di-basic and tri-basic lead acetate.

Sugar of lead comes on to the market in the following forms :—

- | | |
|---|------------------------|
| 1. White sugar of lead, <i>i.e.</i> normal or neutral lead acetate. | |
| 2. Grey sugar of lead, | } Basic sugar of lead. |
| 3. Brown sugar of lead, | |

Sugar of lead is an excellent drier, and is largely used for this purpose, both in paints and varnishes, and is an essential constituent in the patent paste driers, which are so largely used by painters for making their mixed paints dry off quickly.

LEAD RESINATE

Precipitated or Fused

Lead resinate may be made by either of the following processes :—

1. *Precipitation Process.*—Rosin is boiled up with a dilute solution of caustic soda until it is completely saponified. A solution of sugar of lead is then run into the rosin soap solution, and vigorously stirred until all the rosin is completely

precipitated. The precipitated lead resinate (or rosinate) is then well washed with hot water and dried at a low temperature. Precipitated lead resinate is a brownish coloured brittle solid, and as sold usually contains about 17 per cent. lead.

2. *Fusion Process*.—Rosin is melted up in a large pan and finely divided litharge is gradually stirred in at about 300–450° F. Considerable action takes place and the lead dissolves completely in the rosin, forming a bright clear mass. Fused lead resinate comes on to the market in the form of dark-coloured brittle lumps, and contains as a rule about 10 per cent. of metallic lead.

Lead resinate made by the precipitation process may be readily distinguished from the fused lead resinate, as the former always contains traces of moisture.

Lead resinate is soluble in hot linseed oil, wood oil, turpentine or white spirit, and is largely used as a drier for boiling oil as well as a drying agent in the manufacture of varnishes. Dissolved in turpentine, it forms the patent liquid driers which are so largely sold under the name of “terebine.”

LEAD LINOLEATE (Precipitated)

Lead linoleate is prepared by saponifying linseed oil with the requisite amount of weak caustic soda solution, then running in with vigorous stirring a solution of lead acetate. The brownish sticky mass of lead linoleate thus formed is well washed and dried at a low temperature. It is an excellent drier, and is largely used in preference to lead resinate on account of its toughness and elasticity, which far surpasses that of the rather brittle resinate of lead. As a rule it contains about 25 per cent. of metallic lead. It readily dissolves in turpentine, linseed oil, etc.

LEAD TUNGATE (Precipitated)

Prepared from wood oil, or from wood oil fatty acids in a similar manner to that described above under Lead Linoleate.

Lead tungate is an exceedingly powerful drier, and far exceeds in this quality lead linoleate. Of late years it has come into considerable favour as a drier on account of its ready solubility in oils and its property of producing very little “footing” out in the medium in which it is used.

FUSED LEAD LINOLEATE AND TUNGATE

Fused lead linoleates and tungates are produced by dissolving litharge in hot linseed oil or wood oil or their fatty acids. They usually contain about 25–30 per cent. of metallic lead.

MANGANESE DRIERS

MANGANESE DIOXIDE (MnO_2)

(Black Oxide of Manganese.)

Manganese dioxide occurs naturally as pyrolusite and is the raw material from which the various salts of manganese are prepared.

It comes on to the market for use as a drier in the form of a very finely ground black powder containing about 90 per cent. MnO_2 . It is extensively used as a varnish drier, as it requires a fairly high temperature before it will go into solution. Although an exceedingly good drying agent it has unfortunately the drawback that it tends to darken the oils with which it is heated.

On account of only being soluble at comparatively high temperatures it is not used as a paint drier.

MANGANESE SULPHATE (MnSO_4), $5\text{H}_2\text{O}$

This salt is prepared by dissolving manganous oxide or carbonate in sulphuric acid. It is a white salt with a faint pink colour. It is used as a drier in preference to manganese dioxide, as it is more soluble, and, moreover, does not tend to discolour to the same extent as the latter body.

MANGANESE BORATE (MnB_2O_4)

Manganese borate is prepared by dissolving commercially pure manganese sulphate (iron-free) in hot water and adding this solution to a hot solution of borax till no further precipitation takes place.

As the borate of manganese is somewhat soluble in water only one wash should be given; the white precipitate is then filter pressed and dried.

Great care must be taken in precipitating and drying borate of manganese, otherwise the resultant product is dark coloured instead of being perfectly white. Manganese borate when carefully prepared is a white fine light powder, which readily dissolves in linseed or wood oil, etc., at about 300°F ., producing pale oils which dry readily.

It is largely used as a drier both on account of its excellent drying properties and also on account of the fact that it does not discolour the oil to anything like the same extent as the other manganese compounds. For this reason it is almost exclusively used as a drier in the preparation of pale drying oils and varnishes, and also as a constituent of the patent dry or paste zinc white driers, which are employed as driers for white paints and enamels.

The exact composition of pure manganese borate is rather difficult to arrive at, because of the fact that when the precipitated borate is washed it continually loses boric acid. If repeatedly washed the product in drying out turns brown owing to the separation of manganese oxide.

Commercial pure borate of manganese is a white powder which should contain about 19 per cent. of manganese (Mn) and be practically free from alkali. Unfortunately large quantities of borate of manganese are put on to the market which are heavily adulterated with calcium sulphate (terra alba).

As the value of a borate of manganese is dependent not alone on its whiteness but on the amount of manganese it contains, all samples which on analysis contain less than 17-18 per cent. of manganese (Mn) should be rejected (for analysis see page 122, under Manganese).

MANGANESE HYDROXIDE ($\text{Mn}(\text{OH})_2$)

(Brown Oxide of Manganese.)

Manganese hydrate is prepared by adding a weak solution of caustic soda to a solution of manganese chloride or sulphate. The whitish precipitate which first forms readily turns brown and is well washed to remove any excess of alkali; it is then filter pressed and dried at a low temperature.

Manganese hydrate is a darkish brown powder which owing to its greater solubility and non-darkening properties is largely used as a drier in the boiling of oils and the manufacture of varnishes in place of black oxide of manganese.

Burnt umber which has been prepared by gently roasting raw umber till all the moisture has been driven off contains brown oxide of manganese and was formerly extensively used in the preparation of boiled oil and varnishes. Its place in recent years, however, has been taken by the more active chemically prepared driers.

MANGANESE ACETATE ($\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$)

This salt is manufactured by boiling a solution of manganese sulphate with acetate of lime. It is a pinkish crystalline body, which on adding to hot oils or varnishes readily decomposes, giving off acetic acid whilst the manganese goes into solution. It is used to a small extent as a drier, chiefly in the preparation of manganese resins and linoleates.

MANGANESE CHLORIDE (MnCl_2), $4\text{H}_2\text{O}$

Manganous chloride is the final product in all cases where the oxide or carbonate of manganese is treated with hydrochloric acid. It is a pink crystalline salt which readily dissolves in water and is used as a drying agent in patent driers and in the preparation of other manganese driers.

MANGANESE LINOLEATES, TUNGATES AND RESINATES

These may be prepared either by precipitation in the same way as the lead compounds, using manganese sulphate or chloride as the precipitating agents, or else by fusion, cooking manganese acetate into the hot oils or rosin.

Manganese linoleate (precipitated or fused) usually contains about 6 per cent. of manganese; manganese resinates (fused) about 4 per cent., precipitated as a rule about 8 per cent.

The manganese compounds are considerably more powerful driers than the lead compounds, and on this account are used in amounts of about 0.5 per cent. to 1 per cent., whereas in the case of lead a larger quantity is necessary to obtain the same drying effect. The great objection to the use of manganese driers, however, is the darkening action which they exert on the oils in which they are dissolved.

Resinates or linoleates of manganese and lead used together have more powerful

drying properties than either of them used alone; hence it is usual to employ the combined resinates or linoleates in the proportion of about 4 parts of lead to 1 part of manganese to obtain the best drying effect.

COBALT DRIERS

COBALT ACETATE

This is prepared by dissolving cobalt oxide in acetic acid. It is a pinkish coloured crystalline salt which is largely used at the present time as a drier and also in the preparation of cobalt resinates and linoleates by fusion.

It contains usually 23 to 24 per cent. of metallic cobalt (Co), sometimes 27 per cent. to 28 per cent.

COBALT RESINATE

This compound is prepared by cooking cobalt acetate with resin at about 400° F. The best qualities generally contain from 1½ to 2 per cent. cobalt.

It is a very powerful drier, being far superior to lead or manganese resinate, and on this account is very largely used in the preparation of terebines and as a drier for oils and varnishes.

COBALT LINOLEATE

This is prepared by saponifying linseed oil with caustic soda, then adding a dilute solution of cobalt chloride. The cobalt linoleate thus precipitated is well washed and dried at a low temperature.

Cobalt linoleate as usually sold is a dark red sticky substance which contains about 6 per cent. of cobalt. It readily dissolves in turpentine, white spirit, oils, etc., and is very largely used as a drier.

By reason of its very powerful drying properties only very small quantities are required, from 0.25 to 0.5 per cent. being sufficient to dry off an oil or varnish in about eight hours.

The cobalt driers are the most powerful driers known, and at the present time are coming more and more into favour and gradually taking the place of the older lead and manganese driers. They also possess the unique property of bleaching out in the sunlight, which makes them especially valuable as drying agents for white enamels and pale varnishes.

When added to varnishes they do not cause any "footing out" such as is obtained when lead or manganese driers are used.

VANADIUM DRIERS

According to Rhodes & Chen,¹ vanadium driers are only slightly less efficient than cobalt driers. Oils containing vanadium driers dry about twice as rapidly as do oils containing an equivalent amount of manganese drier, and almost five times as rapidly as oils containing an equivalent amount of lead drier. Unfortunately, however, oils treated with vanadium driers are found to be intensely dark in colour. In effective amount the vanadium gives to the oil so dark a colour that its use would

¹ U.S. Paint Manufacturers' Association Circular, 149.

have to be confined to dark coloured paints. The cost of the preparations, moreover, is greater than the cost of cobalt driers, which are really more effective and of very much lighter colour.

The vanadium compounds which may be used as driers are vanadium resinate and linoleate, and are prepared by dissolving ammonium vanadate either in rosin or in linseed oil at a temperature of about 300° C.

TEREBINE (LIQUID DRIER, JAPAN DRIER)

Terebine¹ is a concentrated liquid drier commonly called in America Japan drier, which is largely used as a convenient form of drier to add to liquid paints and varnishes in order to increase their drying properties.

Originally terebine was made by running kauri gum into linseed oil till all taken up, then cooking in a large amount of red lead, litharge, and manganese dioxide till bright, and then thinning out with spirits of turpentine to a thin consistency.

This preparation on drying out gives a hard, tough, lustrous film, and has excellent drying properties. Moreover, it can be mixed in any proportion with white lead or zinc oxide without causing any "livering" or thickening.

At the present time terebines are made by heating the oxides of lead and manganese or borate of manganese with linseed oil or rosin, or mixtures of linseed oil and rosin, at a temperature of about 500° F. till solution takes place and a hard mass is produced, and thinning down with turpentine, white spirit, or mixtures of both, to a thin consistency.

The terebine is tanked and left for a few weeks to brighten, and is then ready for use.

The product thus produced is a dark red coloured thin bright liquid, which has powerful drying properties. It consists of a solution in turpentine or white spirit of lead linoleate, lead resinate, manganese linoleate, manganese resinate, or mixtures of these compounds.

Sometimes, in addition to lead and manganese compounds, compounds of cobalt are used, especially in the preparation of very pale terebines.

A good quality of terebine (liquid drier) should conform to the following specification :—

Specification for Terebine (Liquid Drier)

1. The terebine must be of a clear, transparent, mobile liquid, sweet in odour, and free from any suspended matter or deposit.
2. It should contain about 70–75 per cent. of volatile matter consisting of turpentine or white spirit, or a mixture of these.
3. When the terebine is poured on to glass, in a vertical position, it should dry off in not more than two hours at room temperature, giving a tough, glossy, and clear film.
4. When thoroughly mixed with raw linseed oil at the ordinary temperature,

¹ Terebine must not be confused with terebene, which is an entirely different body (see p. 203).

in proportions of 10 per cent. by volume of terebine to 90 per cent. by volume of raw linseed oil, and allowed to stand for six hours, no separation should occur nor any deposit be formed.

5. When the above mixture is flowed on to glass, placed nearly vertical, the film shall dry off hard at ordinary room temperatures in not more than eighteen hours.

6. When the terebine is mixed with an equal volume of white spirit, a clear solution shall result without residue on standing one hour.

7. The flash point (close test) must not be below 80° F.

8. When the terebine is mixed with white lead or zinc oxide liquid paints, no curdling or "livering" up must take place.

CONCENTRATED DRIERS

These are made by heating linseed oil or rosin to about 300° C. and dissolving in the oxides of lead, manganese or cobalt, or mixtures of these.

They can also be made by the precipitation process by adding solutions of manganese, cobalt and lead salts to solutions of rosin or linseed oil soaps, as described under Lead, Cobalt and Manganese Linoleate or Resinate.

Concentrated driers come on to the market in the form of a dark, thick, viscous mass, or in the case of the resinates, as dark, brittle, solid lumps. They are largely used in the manufacture of oil varnishes and in oil boiling.

Ordinarily they contain the following proportions of lead and manganese, or cobalt:—

Lead and Manganese

Linoleate, precipitated	12 per cent.	Pb, 3 per cent.	Mn
„ fused	12	„ Pb, 3	„ Mn
Resinate, fused	10	„ Pb, 3	„ Mn
„ precipitated	15	„ Pb, 5	„ Mn
Mixed resinate and linoleate	12	„ Pb, 3	„ Mn

Cobalt

Cobalt resinate	2 per cent.	Co.
Cobalt linoleate and resinate	4	„ Co.

DRIERS GROUND IN OIL OR PASTE DRIERS

Paste driers are largely used in the paint trade as a handy form in which driers may be added to paste or liquid paints to increase their drying properties.

They are made by grinding together suitable proportions of barytes, whiting, white lead, sugar of lead, and manganese acetate or chloride in boiled or raw oil. The barytes and whiting simply act as diluents, and, of course, exert no drying action on the paints.

When mixed in suitable proportions—about 7 lbs. to 1 cwt. of paint—to a

white paint they should mix readily without causing any thickening of the paint, and should dry off the paint when it is applied in about twelve hours without any discoloration.

SPECIFICATION FOR DRIERS GROUND IN OIL

The driers, free from oil, must contain suitable lead compounds equivalent to not less than 5 per cent. of lead monoxide (PbO), together with suitable manganese compounds equivalent to not less than 1 per cent. of manganese dioxide (MnO_2).

The suitability of the lead and manganese compounds will be determined by the following drying test :—A thin film of the driers, after thoroughly mixing with an equal part of linseed oil of good quality, must dry to the touch in not more than six hours when exposed in a dry atmosphere at a temperature of approximately 60°F . The composition of the driers must be uniform.

DRY DRIERS, FRENCH DRIERS, ZUMATIO DRIERS, ZINC DRIERS

Dry driers are made by grinding zinc white, manganese borate and whiting together in suitable proportions. They are sold in the form of a dry white powder, and are used for adding to zinc paints, which they should cause to dry off hard without any discoloration.

Compounds of zinc, calcium and aluminium, as the oxides or resinsates, etc., are used as driers in combination with litharge and manganese borate. These bodies are really hardening or neutralising agents, as their drying properties are very small.

ANALYSES OF TEREBINES, LIQUID DRIERS AND CONCENTRATED DRIERS

Estimation of the Volatile Spirit.—5 gms. of the terebine are evaporated to dryness in a sand bath till no more spirit is evolved. Loss of weight equals the amount of volatile matter present.

If an analysis of the thinners is required, then distil off 200 c.c., collect distillate; and test by fractional distillation (see page 198).

Rosin, by the Liebermann-Storch reaction (see page 162).

Lead.—Take 25 gms. of the liquid drier. Remove volatile on the water bath and ignite gently, then strongly. Add hydrochloric acid to ash. Filter and wash with boiling water. Transfer to 6-in. basin and evaporate to small volume. Wash into a beaker and add 200 c.c. of hot distilled water, and pass in sulphuretted hydrogen.

Filter, and without washing transfer to a 3-in. basin and add 25 c.c. of water and a little nitric acid. Cover dish and heat to gentle boil. Filter and wash thoroughly.

To filtrate and washings add 15 c.c. alcohol and dilute sulphuric acid. Stand for two hours with frequent agitations.

Filter through ashless paper, well wash with a mixture of alcohol and water, dry and ignite. Cool and weigh.

Add two or three drops of nitric acid and ignite. Cool and add three drops of sulphuric acid. Ignite and weigh. Equals PbSO_4 , calculate to Pb.

Manganese.—Take filtrate from H_2S . Evaporate to dryness on a water bath. Add a few drops of sulphuric acid, cover basin, and heat gently on a sand bath until sulphuric acid fumes cease to come off. This removes the hydrochloric acid. Cool and add 40 c.c. of water, and boil.

Add paste of zinc oxide (pure) and water in small portions at a time. The zinc oxide precipitates any iron and neutralises the free sulphuric acid.

A small quantity of zinc oxide should remain at the bottom of the dish. Filter and wash.

To the filtrate add 1 or 2 gms. of sodium acetate and heat to nearly boiling. If a good deal of iron is present some may come down at this stage; filter off.

Add slight excess of bromine water and boil cautiously. The manganese is precipitated as manganese dioxide (MnO_2). Filter, wash and ignite and weigh. Equals Mn_2O_3 . Calculate to Mn.

Note.—The above method is also applicable for the estimation of lead and manganese in varnishes.

An alternative method which gives good results is to extract the driers from the terebines, etc., by shaking them in a flask with an equal volume of warm dilute hydrochloric acid for about one hour.

The mixture is then poured into a separating funnel, and the aqueous acid layer, which should contain all the metals present in the medium in solution, is drawn off into a porcelain evaporating dish. The oil portion is washed twice with warm water, adding the washing to the porcelain dish, and evaporating to dryness. The residue consists of the chlorides of all the metals that may be present in the terebine.

The other metals that may be present in a liquid drier (or in a varnish) besides lead and manganese are as follows :—

1. Cobalt. As a general rule if a cobalt salt has been used as the active ingredient the compounds of lead and manganese are absent.
2. Calcium used in the form of lime as a hardening agent for rosin.
3. Alumina in the form of aluminium oleate or linoleate to thicken or body up the oils.
4. Copper if the medium has been prepared in a copper varnish pot.
5. Iron if the medium has been prepared in an iron varnish pot.

Estimation of Cobalt

The cobalt is estimated after the removal of the lead manganese (iron and zinc) by precipitating with ammonia and ammonium sulphide as cobaltous sulphide; dissolving this precipitate in nitric acid, adding H_2SO_4 , taking down nearly to dryness, then diluting with water, making almost neutral with ammonia, and precipitating with a boiling hot concentrated solution of ammonium hydrogen phosphate.

The precipitate is washed, dried and weighed as CoNH_4PO_4 . The other metals, such as iron, copper, zinc, alumina and calcium, are estimated if required by the usual methods of analysis, which need not be described in detail.

Cobalt Resinate, Cobalt Linoleate, Cobalt Acetate, etc.

The percentage of metallic cobalt present in concentrated or solid cobalt driers may be estimated as follows :—

Ash 1 gm. of the sample in a crucible. Dissolve in hydrochloric acid and filter. Add 5 c.c. sulphuric acid and evaporate to dryness in a porcelain evaporating dish and weigh as cobalt sulphate. Calculate to metallic cobalt.

An alternative method consists in precipitating the cobalt as hydroxide, drying the precipitate, and igniting in a current of hydrogen gas, and weighing the metallic cobalt thus produced.

CHAPTER XXI

BRUNSWICK BLACKS, BLACK JAPANS AND STOVING BLACKS

THE manufacture of bituminous coatings for the protection of iron and stone work from the action of moisture, and also for production of matt or highly lustrous black surfaces in coach work, is an important branch of the varnish industry.

The range of black varnishes manufactured is very large, and their composition and properties as regards toughness and elasticity and time of drying varies greatly according to the purpose for which they are intended to be used.

They may dry off at the ordinary temperature in a few minutes, or, on the other hand, high stoving temperatures maintained over a period of from two to three hours may be necessary before the desired hardness of finish is attained.

These black varnishes are prepared so that in drying off they produce flat, egg-shell gloss, or high gloss finishes. The raw materials mainly used in the manufacture of black varnishes are :—

- (1) Natural asphaltum or bitumen, Gilsonite, Manjak.
- (2) Artificial pitches such as—
 - Bone pitches.
 - Coal tar pitches.
 - Stearin pitches.
 - Petroleum pitches.
 - Wood tar pitches, Waza pitch, rosin pitch, etc.
- (3) Varnish gums.

(1) ASPHALTUM

Natural asphalt or bitumen is imported from various places. It occurs in almost inexhaustible quantity in the great asphalt lake in the island of Trinidad, as also in North America, Mexico, Cuba, Syria, etc. It is a blackish brown, lustrous and brittle solid, breaking with a conchoidal fracture. Its specific gravity varies from 1.07 to 1.17.

Asphaltum, the best variety of which is known as Manjak, melts at about 100° C., giving off a thick brownish vapour with a nasty characteristic smell. On ignition it burns with a bright smoky flame, leaving a little ash. It is soluble in turpentine, benzol, carbon disulphide and chloroform.

Asphaltum is generally considered to be a solid polymerised product of petroleum.

Gilsonite is a hard, lustrous, black bitumen having a specific gravity of about 1.04 and melts at about 300° F.

It is not equal in staining properties to Manjak.

The genuine asphaltums have a fixed carbon content of about 15 per cent. to 20 per cent., and are quite unsaponifiable.

(2) ARTIFICIAL PITCHES

Various artificial pitches, such as coal tar pitch, bone pitch, stearin pitch, petroleum pitch, etc., are used also either alone or in conjunction with asphaltum for the manufacture of black varnishes. These artificial pitches vary considerably as regards their properties, *e.g.* bone pitch is a very dense black brittle product, and is used chiefly on account of its blackness with a softer pitch, such, for instance, as stearin pitch.

Petroleum pitches vary in consistency from solid to semi-liquid, and are employed chiefly in the manufacture of the cheaper black varnishes.

(3) VARNISH GUMS

Various copal gums in combination with linseed oil are used in the manufacture of high-class black Japans to impart lustre and durability to these products. In the case of the cheaper quick-drying asphaltum varnishes common rosin is also used to increase their lustre, but this is not looked on with favour on account of its tendency to make the coating brittle.

BRUNSWICK BLACK

This asphaltum black varnish is very largely used for coating iron work in order to protect the metal from rusting and to give a high lustrous black finish. It may be made according to the following general formulæ (Livache) :—

1	2
Asphaltum ⁷ . . . 2 parts	Asphaltum . . . 1 part
Spirits of turpentine . . . 3½ „	Boiled linseed oil . . . 3-6 parts
	Spirits of turpentine . . . 2-4 „

COMMON BLACK VARNISH

Cheap black varnish for wood and iron work for common outside use consists of coal tar pitch dissolved in heavy coal tar naphtha; sometimes a mixture of creosote oil and naphtha is used. It dries in about four to sixteen hours, according to the purpose for which it is intended, and is an excellent protective coating against all weathering influences.

EXTRA QUICK-DRYING BLACK VARNISH

These varnishes can be made to dry off in about ½ to 1 hour, and are prepared by dissolving asphaltum in low flash spirit such as benzol, benzine or shale spirit.

BLACK JAPANS

Black Japans are used mainly in high-class coach work, and are high-grade asphaltum varnishes to which a proportion of hard drying copal varnish has been added to impart lustre and durability.

They should dry off hard in a few hours and when varnished over should not show any "greening" effect.

The asphaltum used in this class of varnishes should be of the best quality, hard and lustrous, and of as dense a black as possible. Sweated pitches such as Waza pitch are also used, and a little Prussian blue is usually added to increase the blackness of the finished Japan.

The following formulæ will give a general idea as to the way in which these black Japans may be prepared.

1	2
Asphaltum . . . 50 lbs.	Asphaltum . . . 10 lbs.
Linseed oil . . . 10 gals.	Sweated Waza pitch . . . 40 „
Litharge . . . 4 lbs.	Boiled oil . . . 3 gals.
Red lead . . . 4 „	Red lead . . . 4 lbs.
Hard animi varnish . . . 5 gals.	Hard carriage varnish . . . 10 gals.
Turpentine . . . 30 gals.	Turpentine . . . 20 „
	Prussian blue . . . 3 ozs.

The asphaltum, etc., is melted up in a large iron pot with the linseed oil, and the driers cooked in till a portion taken out forms a very hard mass. The pot is allowed to cool sufficiently and then thinned down to the right consistency with spirits of turpentine. The varnish is finally stirred well in and the Japan strained and tanked.

STOVING BLACKS OR BAKING JAPANS

This class of goods is largely used in the cycle and bedstead trades, and is usually applied either by dipping or spraying.

The coated articles are stoved at temperatures varying from 150–400° F., according to the particular nature of the Japan used.

The Japans after stoving form very hard, tough and exceedingly durable coatings on the metal objects on which they are applied. They are manufactured by cooking linseed oil with litharge, red lead, and black oxide of manganese till it is oxidised to almost a solid mass (lead oil). Stearin pitch, and a little bone pitch, to increase the blackness of the finished black, are next added to the hot oil mass, and thoroughly cooked until all are amalgamated. The black is then thinned down to the right consistency with kerosine, strained and tanked till all impurities have settled out.

FLAT DRYING BLACK JAPANS

Black drying Japans, either stoving or air drying, are prepared so as to give a matt or egg-shell finish. They are made by adding vegetable black to the ordinary black Japans in sufficient quantity to give the desired finish, enough volatile thinner being added to reduce the product to good working consistency.

Analysis of Black Japans

The analysis of a black Japan so as to differentiate the various constituents, together with their percentages, is not practicable.

It is, however, quite sufficient if the Japan under examination is compared with various other standard Japans as to its working properties, finish, time of drying, etc., as by this means comparative results may be obtained which enable it to be identified and related to the class to which it belongs.

Also no general specification can be given for these black Japans, as they vary so much according to the purposes for which they are to be employed.

BIBLIOGRAPHY

- Handbuch der Farbenfabrikation. Von Georg Zerr und Dr R. Rubencamp. (3rd Edition, Union Deutsche Verlagsgesellschaft, Berlin.)
- Painters' Colours, Oils and Varnishes. 5th Edition. By C. H. Hurst. (Griffin & Co., 1913.)
- The Manufacture of Paint. By J. Cruickshank Smith. (Scott, Greenwood & Son.)
- Paint and Colour Mixing. By Arthur Seymour Jennings. (E. & F. N. Spon, Ltd., London.)
- Analysis of Paint Vehicles, Japans and Varnishes. By Clifford Dyer Holley. (John Wiley & Sons, Inc., New York, 1920.)
- Analysis of Paint and Varnish Products. By Clifford Dyer Holley. (John Wiley & Sons, New York.)
- Various Points in the Manufacture of Lake and Pigment Colours. By J. B. Shaw. (Journal of the O. and C. C. Assoc., April 1920.)
- Iron-corrosion, Anti-fouling and Anti-corrosive Paints. By Louis Edgar Andes. (Scott, Greenwood & Son.)
- The Analysis and Valuation of Paints, Varnishes and Enamels. By A. de Waele. (Journal of the O. and C. C. Assoc., April 1920.)
- Fineness and Texture of Pigments. H. A. Gardner. (Educational Bureau, Washington, Circular No. 90, March 1920.)
- Paint a Plastic Material and not a Viscous Liquid. Bingham and Green. (American Soc. for Testing Materials, 22nd Annual Meeting, June 1919.)
- Technology of Paint and Varnish. By Sabin. (John Wiley & Sons.)
- The Chemistry of Paints and Paint Vehicles. By Hall.
- The Chemistry of Paints and Painting. By A. H. Church. (Seeley & Co., Ltd., London.)
- The Chemistry of Pigments. By E. J. Parry and J. H. Coste. (Scott, Greenwood & Son.)
- The Chemistry of Linseed Oil. By J. Newton Friend. (Gurney & Jackson, 1917.)
- German Varnish Making. By Prof. Max Bottler, translated with Notes on American Varnish and Paint Manufacture by Aloah Horton Sabin. (John Wiley & Sons, New York.)
- Casein: Its Preparation and Technical Utilisation. By Robert Scherer. (3rd English Edition, 1921, revised and enlarged by H. B. Stocks.) (Scott, Greenwood & Son, London.)
- Manufacture of Varnishes and Kindred Industries. Livache.
- Bestimmung von Teerfarbstoffen in Farblacken. Von Georg Zerr. (Union Deutsche Verlagsgesellschaft, Berlin, 1922.)
- Chemie der organischen Farbstoffen. Von Prof. Dr Rudolf Nietzki. (Springer, Berlin.)
- Die Anilinfarben und ihre Fabrikation. Von Dr K. Heumann, fortgesetzt von Dr Paul Friedländer. (Vieweg & Sohn.)
- Die neuern Farbstoffe der Pigmentfarbenindustrie. Von Dr C. Staebble. (Berlin.)
- Analysis of Oil Varnishes. (Proc. Am. Soc. for Test. Mat. 8, 1908.)
- Evaluation of White Pigments, with Special Reference to Antimony Oxide. By H. E. Clarke. (Journal of the Oil and Colour Chemists' Assoc., vol. iv., Jan. 1921.)

- Titanium White: Its Production, Properties and Use. (Journal of the Oil and Colour Chemists' Assoc., 1921.)
- Lacquer Industry of Japan. J. J. Quinn. (British Consular Reports, 188.)
- Polymerised Drying Oils. (J. Soc. Chem. Ind., 1915.)
- A Contribution to the Analysis of Oil Varnishes. Wolff. (Farben Zeitung, 1916.)
- Analysis of Oil Varnishes. McIlhiney. (Proc. Am. Soc. for Test. Mat. 8, p. 596, 1908.)
- Die Chemie der austrocknenden Öle. By Mulder. (Berlin, 1867.)
- Rubber Seed Oil and a Method of producing Glycerides from Fatty Acids. H. A. Gardner. (Paint Manufacturers' Assoc. of the U.S., Circular No. 118.)
- Carbon Black: Its Properties and Uses. By G. St J. Perrott and Reinhardt Thiessen. (Journal Ind. and Eng. Chem., xii. 324, 1920.)
- Fineness and Texture of Pigments. H. A. Gardner. (Educational Bureau, Washington, Circular No. 90, March 1920.)
- Determination of Volatile Thinners in Oil Varnishes. De Waele and F. Smith. (Analyst, 1917, 42, p. 170.)
- Analysis of Resins, Balsams and Gum Resins. Dietrich. (1901.)
- Oxidation of Oils. Ingle. (J. Soc. Chem. Ind., p. 639, 1913.)
- Shellac. By A. F. Suter. (Jour. Royal Soc. Arts, 57, 660.)
- Nitrocellulose Industry. By E. C. Worden. 2 vols. (1911.)
- Testing American Aeroplane Varnish. By C. Webb. (Paint, Oil and Drug Review, Chicago, May 1919.)
- Turpentine: Its Sources, Properties and Uses. (United States Department of Agriculture, Bulletin No. 898.)
- Varnishes from Wood Oil and Rosin. (O. and C. Trades Journal, July 1917.)
- Pyroxyline. G. Lunge. (Z. Angew. Chem., xxix., 2051-58.)
- The Analysis of Prussian Blue. Parry and Coste. (The Analyst, xxi. 225-230. 1896.)
- White Lead. W. A. Davis and C. A. Klein. (J. Soc. Chem. Ind., xxvi. 848.)
- Technologie der Fette und Öle. By Gustav Heffer. (Berlin, 1921.)
- Die Chemie der trocknenden Öle. By Dr Fahrion. (Berlin, 1911.)
- Technical Handbook of Oils, Fats and Waxes. By Percival J. Fryer and Frank E. Weston. (Cambridge University Press.)
- The Testing of Chemical Reagents for Purity. Dr G. Krauch. Translated by J. A. Williamson and L. W. Dupré. (MacLaren & Sons, London.)
- Chemical Analysis of Oils, Fats and Waxes. By Dr J. Lewkowitsch. (Macmillan & Co.)
- The Manufacture of Lake Pigments from Artificial Colours. By Francis H. Jenninson. 2nd Edition. (Scott, Greenwood & Son.)
- The Manufacture of Earth Colours. By Josef Bersch. (Scott, Greenwood & Son.)
- A Practical Treatise of the Manufacture of Colours for Painting. Revised by M. F. Malepeyre, translated by A. A. Fesquet. (Philadelphia, 1874.)
- Air Ministry Cellulose Acetate Dope (3 D100). (British Standard and Air Board Specifications for Aircraft Materials, 1st Nov. 1922.)
- Nitro-cellulose Dope (D102). (British Standard and Air Board Spec., etc.)
- Properties of Aeroplane Dope. (British Standard and Air Board Spec., etc.)
- Handbuch der Lack- und Firnisindustrie von Seeligmann und Zicke, Dritte Auflage. (Berlin, 1923.)
- Die Anstrichfarben und ihre Bindemittel im Farbenhandel. Von W. Antony. (Berlin, 1923.)

APPENDIX

1921

INTERNATIONAL ATOMIC WEIGHTS

	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.9	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation)	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.008
Boron	B	10.9	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Cæsium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.9
Chlorine	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.1	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	45.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	70.1	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.06
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.00	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.15
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	173.5
Lutecium	Lu	175.0	Yttrium	Yt	89.33
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

WEIGHTS AND MEASURES

MEASURES OF WEIGHT

Grains.	Grams.	Ozs.	Lbs.	Cwt.
1	·064799	..	·000143	..
15·4326	1	·03527	·002204	..
437·5	28·3495	1	·0625	·000558
7000	453·59	16	1	·00893
..	50802·35	1792	112	1

1 cwt.=50·8024 kg. 1 kg.=2·2046223 lbs.

1 metric ton=1000 kgs.=2,204·622 lbs.=·9842 imperial ton.

1 imperial ton=1,016,047 grams=2,240 lbs.=1·016 metric ton.

LINEAR MEASURE

Ins.	Ft.	Yds.	Miles.	Cm.	Metre.	Km.
1	·083	·02778	·0000158	2·5399978	·0254	1·0000254
12	1	·333	·0001894	30·47997	·3048	·0003048
36	3	1	·000568	91·44	·9144	·0009140
63360	5280	1760	1	1609315	1609·315	1·609315
·393701	1
39·3701	3·280843	1·093614	..	100	1	·001
..	..	1093·61426	·62137	100,000	1000	1

SQUARE MEASURE

1 sq. in. =6·451589 sq. cm.	1 sq. dm.= 15·50006 sq. ins.
1 sq. ft. =9·29029 sq. dm.	1 sq. m. = 10·7693 sq. ft.
1 sq. yd. = ·836126 sq. m.	1 sq. m. = 1·195992 sq. yds.
1 acre = 4840 sq. yds.	1 are =119·59921 sq. yds.
1 acre = ·40468 hectare	1 are = ·0247106 acres
640 acres=1 mile	

CUBIC MEASURE

1 c.c. = ·061024 cu. ins.	1 cu. in. =16·38702 cu. cm. (cm ³).
1 cu. (m ³)=35·31476 cu. ft.	1 cu. ft. =28·31677 cu. dm. (d.m ³).
1 cu. = 1·3907954 cu. yds.	1 cu. yd. = ·76455285 cu. m. (m ³).
1 cu. in. of water at 62° F. weighs	·036041 lbs.
1 " " " " " "	252·286 grains.
1 cu. ft. " " " " "	996·458 ozs.
1 " " " " " "	62·2786 lbs.

MEASURE OF VOLUME

Cu. cm.	Litres.	Cu. in.	Cu. ft.	Fl. oz.	Pint.	Gallons.
1	..	·061027	..	·0352	·00176	..
1000	1	61·0349	·035216	35·196	1·761	·220096
16·387	·0164	1	..	·577	·02885	..
28315·3	28·3153	..	1	997·1364	49·8569	6·2321
28·396	..	1·7329	..	1
567·919	·56825	34·659	..	20 (water)	1	·125
4545·96	4·54596	277·274	..	160	8	1

1 c.c.=·282 fl. drams.

MENSURATION OF REGULAR FIGURES

Area of a triangle= $\frac{1}{2}$ base \times height.

Area of a parallelogram=base \times perpendicular height.

Area of a trapezium=half the sum of the parallel sides \times the perpendicular distance between them.

Area of a sector A B C of a circular is $\frac{1}{2}$ (arc B C) \times (radius)= $\frac{1}{2} r\theta$. $r=r^2\theta$. Where θ is the angle of the sector measured in radians.

Volume of pyramid= $\frac{1}{3}$ (area of base) \times (height)= $11rl$.

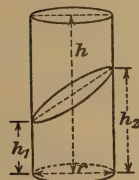
The portion of a pyramid or cone cut off by a plane parallel to the base is called a frustum.

Volume of a frustum of a pyramid

$$= \frac{h}{3} (A + \sqrt{AB} + B),$$

where h is the height and A and B are the areas of the two parallel faces.

If r_1 and r_2 are the radii of the two parallel faces of a frustum of a cone, then $A=\pi r_1^2$, $B=\pi r_2^2$, and the volume of a frustum of a cone= $\frac{\pi h}{3} (r_1^2 + r_1 r_2 + r_2^2)$.

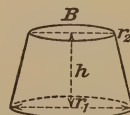
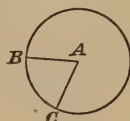


Cylinder

Volume of a cylinder= $\pi r^2 h$.

Volume of a frustum of a cylinder= $\pi r^2 \frac{h_1 + h_2}{2}$.

If r is the internal and R the external radius of a hollow cylinder or pipe, the volume is the difference between the volume of the external cylinder and that of the internal cavity= $\pi R^2 h - \pi r^2 h = \pi h (R^2 - r^2)$.



COMPARISON OF FAHRENHEIT AND CENTIGRADE THERMOMETERS

°C	F°	°C	F°	°C	F°	°C	F°
-10	14	55	131	120	248	240	464
-5	23	60	140	130	266	250	482
0	32	65	149	140	284	260	500
+5	41	70	158	150	302	270	518
10	50	75	167	160	320	280	536
15	59	80	176	170	338	290	554
20	68	85	185	180	356	295	563
25	77	90	194	190	374	300	572
30	86	95	203	200	392	325	617
35	95	100	212	210	410	350	642
40	104	105	221	220	428	375	667
45	113	110	230	230	446	400	692
50	122						

To convert—

Rules

°F into °C—First subtract 32, then multiply by 5 and divide by 9.

°F into °R—First subtract 32, then multiply by 4 and divide by 9.

°C into °F—Multiply by 9, divide by 5, then add 32.

°C into °R—Multiply by 4 and divide by 5.

°R into °F—Multiply by 9 and divide by 4, then add 32.

°R into °C—Multiply by 5 and divide by 4.

FACTORS REQUIRED IN GRAVIMETRIC ANALYSIS

Element.	To convert	into	Multiplier.
Al	Al ₂ O ₃	Al ₂	0.5294
	"	Ammonia Alum	8.8824
	"	Potash Alum	9.2941
As	As ₂ S ₃	As ₂ O ₃	0.8049
	As ₂ O ₃	As ₂	0.7576
Ba	BaSO ₄	Na ₂ SO ₄ ·10H ₂ O	1.382
	"	MgSO ₄	0.515
	"	PbSO ₄	1.3
	"	SO ₃	0.3434
	"	S	0.1373
Ca	CaO	CaSO ₄ ·2H ₂ O	3.0715
	"	CaCO ₃	1.784
	CaCO ₃	CO ₂	0.440
	CaSO ₄ ·2H ₂ O	SO ₃	0.4561
C	CO ₂	CaCO ₃	2.2727
Cr	Cr ₂ O ₃	PbCrO ₄	3.230
	Cr ₂ O ₃	CrO ₃	1.3137
Fe	Fe	FeO	1.2857
	Fe ₂	Fe ₂ O ₃	1.4286
	Fe ₂ O ₃	Fe ₂	0.7
Mg	Mg ₂ P ₂ O ₇	Mg ₂	0.2162
	"	2MgO	0.3604
	"	2MgCO ₃	0.7568

Element.	To convert	into	Multiplier.
	$\text{Mg}_2\text{As}_2\text{O}_7$	As_2	0.4839
	$\text{Mg}_2\text{As}_2\text{O}_7$	As_2O_3	0.6387
Na	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	Na_2O	0.4366
Pb	Pb	PbO	1.0733
	PbS	Pb	0.8658
	PbSO_4	Pb	0.6826
	PbCrO_4	Pb	0.6406
	PbSO_4	PbO	0.7355
	PbSO_4	$\text{Pb}(\text{NO}_3)_2$	1.092
Sb	Sb_2S_3	Sb_2	0.7143
Zn	ZnO	Zn	0.8025
	ZnS	Zn	0.6701

Addenda

Al	Alumina (Al_2O_3)	China Clay	2.5372
	China Clay	Silica (SiO_2)	0.4667
C	CO_2	White Lead	8.8068
Fe	Fe	Prussian Blue	3.03
N	N	"	4.4
Pb	PbSO_4	White Lead	0.8526

STANDARD SOLUTIONS REQUIRED IN VOLUMETRICAL ANALYSIS

 $\frac{\text{N}}{\text{I}}$ Solutions.

Substance.	Formula.	Weight.
Hydrochloric Acid . . .	HCl . . .	36.5 gms. per litre.
Nitric Acid . . .	HNO_3 . . .	63 " "
Sulphuric Acid . . .	H_2SO_4 . . .	49 " "
Caustic Soda . . .	NaOH . . .	40 " "
Caustic Potash . . .	KOH . . .	56 " "
Sodium Carbonate . . .	Na_2CO_3 . . .	53 " "
Potassium Iodide . . .	KI . . .	166 " "
Oxalic Acid . . .	COOH . . .	63 " "
	COOH $+2\text{H}_2\text{O}$	

 $\frac{\text{N}}{2}$ Solutions.

Potassium Ferrocyanide . . .	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. . .	52.75 " "
Potassium Cyanide . . .	KCN . . .	32.50 " "
Arsenious Oxide . . .	As_2O_3 . . .	49.50 " "

 $\frac{\text{N}}{10}$ Solutions.

Potassium Dichromate . . .	$\text{K}_2\text{Cr}_2\text{O}_7$. . .	4.9033 " "
Potassium Permanganate . . .	KMnO_4 . . .	3.160 " "
Sodium Thiosulphate . . .	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. . .	24.8 " "
Iodine . . .	I_2 . . .	12.7 " "
Silver Nitrate . . .	AgNO_3 . . .	16.966 " "

MULTIPLIERS REQUIRED IN VOLUMETRIC ANALYSIS

Iron (Fe)=56.

1 c.c. $\frac{N}{10}$ KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_4$, or Hyposulphite=0.0056 gms. of Fe=0.0072 gms. $\frac{1}{2}\text{FeO}$ =
0.0080 gms. Fe_2O_3 .

Chlorine (Cl)=35.5.

1 c.c. $\frac{N}{10}$ AgNO_3 =0.00355 gms. of Cl=0.005845 gms. NaCl.

Iodine (I)=127

1 c.c. $\frac{N}{10}$ Hyposulphite=0.0127.

1 c.c. $\frac{N}{10}$ Iodine=0.0060 gms. Sb=0.0072 gms. Sb_2O_3 .

Oxalic Acid $\left(\frac{\text{COOH}}{\text{COOH}} 2\text{H}_2\text{O}=126\right)$.

1 c.c. $\frac{N}{10}$ KMnO_4 =0.0063 gms. $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ =0.0045 gms. $\text{C}_2\text{H}_2\text{O}_4$.

TWADDELL AND BEAUMÉ DEGREES AND EQUIVALENT SPECIFIC GRAVITIES

°B.	°Tw.	Sp. Gr.	°B.	°Tw.	Sp. Gr.	°B.	°Tw.	Sp. Gr.	°B.	°Tw.	Sp. Gr.
1	1.4	1.007	18	28.4	1.142	35	64	1.320	51	109.2	1.546
2	2.8	1.014	19	30.4	1.152	36	66.4	1.332	52	112.6	1.563
3	4.4	1.022	20	32.4	1.162	37	69	1.345	53	116.0	1.580
4	5.8	1.029	21	34.2	1.171	38	71.4	1.357	54	119.4	1.597
5	7.4	1.037	22	36.0	1.180	39	74	1.370	55	123.0	1.615
6	9.0	1.045	23	38.0	1.190	40	76.6	1.383	56	127.0	1.635
7	10.2	1.052	24	40	1.200	41	79.4	1.397	57	130.4	1.652
8	12.0	1.060	25	42	1.210	42	82	1.410	58	134.2	1.671
9	13.4	1.067	26	44	1.220	43	84.8	1.424	59	138.2	1.691
10	15.0	1.075	27	46.2	1.231	44	87.6	1.438	60	142.0	1.710
11	16.6	1.083	28	48.2	1.241	45	90.6	1.453	61	146.4	1.732
12	18.2	1.091	29	50.4	1.252	46	93.6	1.468	62	150.6	1.753
13	20.0	1.100	30	52.6	1.263	47	96.6	1.483	63	155.0	1.775
14	21.6	1.108	31	54.8	1.274	48	99.6	1.498	64	159.0	1.795
15	23.2	1.116	32	57	1.285	49	103.0	1.515	65	164.0	1.820
16	25.0	1.125	33	59.4	1.297	50	106.0	1.530	66	168.4	1.842
17	26.8	1.134	34	61.6	1.308						

Hydrometers

$$\text{Sp. Gr.} = 1 + \frac{^\circ\text{Tw} \times 5}{1000} \qquad ^\circ\text{Twaddell} = \frac{(\text{Sp. Gr.} - 1) \times 1000}{5}$$

For liquids denser than water

$$\text{Sp. Gr.} = \frac{144}{144 - ^\circ\text{Be}} \qquad ^\circ\text{Beaumé} = 144 - \frac{144}{\text{Sp. Gr.}}$$

For liquids less dense than water.

$$\text{Sp. Gr.} = \frac{144}{^\circ\text{Be.} + 134} \qquad ^\circ\text{Beaumé} = \frac{144}{\text{Sp. Gr.} - 134}$$

THE SPECIFIC GRAVITY OF ACETIC ACID AT 15° C.

Per cent.	Sp. Gr.	Per cent.	Sp. Gr.	Per cent.	Sp. Gr.	Per cent.	Sp. Gr.	Per cent.	Sp. Gr.	Per cent.	Sp. Gr.
0	0.9992	17	1.0242	34	1.0459	51	1.0623	68	1.0725	85	1.0739
1	1.0007	18	1.0256	35	1.0470	52	1.0631	69	1.0729	86	1.0736
2	1.0022	19	1.0270	36	1.0481	53	1.0638	70	1.0733	87	1.0731
3	1.0037	20	1.0284	37	1.0492	54	1.0646	71	1.0737	88	1.0726
4	1.0052	21	1.0298	38	1.0502	55	1.0653	72	1.0740	89	1.0720
5	1.0067	22	1.0311	39	1.0513	56	1.0660	73	1.0742	90	1.0713
6	1.0083	23	1.0324	40	1.0523	57	1.0666	74	1.0744	91	1.0705
7	1.0096	24	1.0337	41	1.0533	58	1.0673	75	1.0746	92	1.0696
8	1.0113	25	1.0350	42	1.0543	59	1.0679	76	1.0747	93	1.0686
9	1.0127	26	1.0363	43	1.0552	60	1.0685	77	1.0748	94	1.0674
10	1.0142	27	1.0375	44	1.0562	61	1.0691	78	1.0748	95	1.0660
11	1.0157	28	1.0388	45	1.0571	62	1.0697	79	1.0748	96	1.0644
12	1.0171	29	1.0400	46	1.0580	63	1.0702	80	1.0748	97	1.0625
13	1.0185	30	1.0412	47	1.0589	64	1.0707	81	1.0747	98	1.0604
14	1.0200	31	1.0424	48	1.0598	65	1.0712	82	1.0746	99	1.0580
15	1.0214	32	1.0436	49	1.0607	66	1.0717	83	1.0744	100	1.0553
16	1.0228	33	1.0447	50	1.0615	67	1.0721	84	1.0742		

Note.—The specific gravities above 1.0553 in each case represent two liquids of very different strength.

In order to ascertain whether the acid exceeds the maximum density (78 per cent.) or the reverse, it suffices to add a little water; in the case of stronger acid the specific gravity increases, and decreases if the acid is weaker.

SULPHURIC ACID

SPECIFIC GRAVITY AND CONCENTRATION OF ITS SOLUTIONS

Sp. Gr. at 15/4°	H ₂ SO ₄ per cent.	Sp. Gr. at 15/4°	H ₂ SO ₄ per cent.	Sp. Gr. at 15/4°	H ₂ SO ₄ per cent.	Sp. Gr. at 15/4°	H ₂ SO ₄ per cent.
1.005	0.83	1.240	32.28	1.480	57.83	1.720	78.92
1.020	3.03	1.260	34.57	1.500	59.70	1.740	80.68
1.040	5.96	1.280	36.87	1.520	61.59	1.760	82.44
1.060	8.77	1.300	39.19	1.540	63.43	1.780	84.50
1.080	11.60	1.320	41.50	1.560	65.08	1.800	86.90
1.100	14.35	1.340	43.74	1.580	66.71	1.820	90.05
1.120	17.01	1.360	45.88	1.600	68.51	1.827	91.50
1.140	19.61	1.380	48.00	1.620	70.32	1.834	93.05
1.160	21.19	1.400	50.11	1.640	71.99	1.839	95.00
1.180	24.76	1.420	52.15	1.660	73.64	1.8415	97.00
1.200	27.32	1.440	54.07	1.680	75.42	1.8400	98.70
1.220	29.84	1.460	55.97	1.700	77.17	1.8385	99.95

TABLE SHOWING THE STRENGTHS OF NITRIC ACID OF
DIFFERENT DENSITIES

Sp. Gr. at 15° C.	HNO ₃ per cent.	Sp. Gr. at 15° C.	HNO ₃ per cent.	Sp. Gr. at 15° C.	HNO ₃ per cent.	Sp. Gr. at 15° C.	HNO ₃ per cent.
1.020	3.70	1.170	27.88	1.320	50.71	1.470	82.90
1.030	5.50	1.180	29.38	1.330	52.37	1.480	86.05
1.040	7.26	1.190	30.88	1.340	54.07	1.490	89.60
1.050	8.99	1.200	32.36	1.350	55.79	1.500	94.09
1.060	10.68	1.210	33.82	1.360	57.57	1.502	95.08
1.070	12.33	1.220	35.28	1.370	59.39	1.504	96.00
1.080	13.95	1.230	36.78	1.380	61.27	1.506	96.76
1.090	15.53	1.240	38.29	1.390	63.23	1.508	97.50
1.100	17.11	1.250	39.82	1.400	65.30	1.510	98.10
1.110	18.67	1.260	41.34	1.410	67.50	1.512	98.53
1.120	20.23	1.270	42.87	1.420	69.80	1.514	98.90
1.130	21.77	1.280	44.41	1.430	72.17	1.516	99.21
1.140	23.31	1.290	45.95	1.440	74.68	1.518	99.46
1.150	24.84	1.300	47.49	1.450	77.28	1.520	99.67
1.160	26.36	1.310	49.07	1.460	79.98		

TABLE SHOWING THE STRENGTH OF HYDROCHLORIC ACID OF
DIFFERENT DENSITIES

Sp. Gr. at 15° C.	HCl per cent.	Sp. Gr. at 15° C.	HCl per cent.	Sp. Gr. at 15° C.	HCl per cent.	Sp. Gr. at 15° C.	HCl per cent.
1.005	1.15	1.055	11.18	1.105	20.97	1.155	30.55
1.010	2.14	1.060	12.19	1.110	21.92	1.160	31.52
1.015	3.12	1.065	13.19	1.115	22.86	1.165	32.49
1.020	4.13	1.070	14.17	1.120	23.82	1.170	33.46
1.025	5.15	1.075	15.16	1.125	24.78	1.175	34.42
1.030	6.15	1.080	16.15	1.130	25.75	1.180	35.39
1.035	7.15	1.085	17.13	1.135	26.70	1.185	36.31
1.040	8.16	1.090	18.11	1.140	27.66	1.190	37.23
1.045	9.16	1.095	19.06	1.145	28.61	1.195	38.16
1.050	10.17	1.100	20.01	1.150	29.57	1.200	39.11

TABLE GIVING STRENGTHS OF SOLUTIONS OF CAUSTIC SODA AND POTASH
BY THEIR SPECIFIC GRAVITY

Sp. Gr.	Per cent. NaOH	Per cent. KOH	Sp. Gr.	Per cent. NaOH	Per cent. KOH	Sp. Gr.	Per cent. NaOH	Per cent. KOH
1.0070	0.61	0.90	1.1520	13.55	17.60	1.3458	31.22	34.90
1.0141	1.20	1.70	1.1613	14.37	18.60	1.3585	32.47	35.90
1.0213	2.00	2.60	1.1707	15.13	19.50	1.3714	33.69	36.90
1.0286	2.71	3.50	1.1803	15.91	20.50	1.3846	34.96	37.80
1.0360	3.35	4.50	1.1901	16.77	21.40	1.3981	36.25	38.90
1.0435	4.00	5.60	1.2000	17.67	22.50	1.4187	38.13	40.40
1.0511	4.64	6.40	1.2101	18.58	23.30	1.4328	39.39	41.50
1.0588	5.29	7.40	1.2202	19.58	24.20	1.4472	40.75	42.75
1.0667	5.87	8.20	1.2308	20.59	25.10	1.4619	42.12	44.00
1.0746	6.55	9.20	1.2414	21.42	26.10	1.4769	43.66	45.20
1.0827	7.31	10.10	1.2522	22.64	27.00	1.4845	44.38	45.80
1.0909	8.00	10.90	1.2632	23.67	28.00	1.4922	45.27	46.45
1.0100	8.68	12.00	1.2743	24.81	28.90	1.5000	46.15	47.10
1.1077	9.42	12.90	1.2857	25.80	29.80	1.5079	46.87	47.70
1.1163	10.06	13.80	1.2973	26.83	30.70	1.5158	47.60	48.30
1.1250	10.97	14.80	1.3001	27.80	31.80	1.5238	48.81	48.85
1.1339	11.84	15.70	1.3211	28.83	32.70	1.5319	49.02	49.40
1.1423	12.64	16.50	1.3333	29.93	33.70			

SPECIFIC GRAVITIES OF AQUEOUS AMMONIA

Sp. Gr. 15° C.	NH ₃ per cent.	Sp. Gr. 15° C.	NH ₃ per cent.	Sp. Gr. 15° C.	NH ₃ per cent.	Sp. Gr. 15° C.	NH ₃ per cent.	Sp. Gr. 15° C.	NH ₃ per cent.
.996	0.91	.972	6.80	.948	13.31	.924	20.49	.900	28.33
.994	1.37	.970	7.31	.946	13.88	.922	21.11	.898	29.00
.992	1.84	.968	7.82	.944	14.46	.920	21.75	.896	29.69
.990	2.31	.966	8.33	.942	15.04	.918	22.38	.894	30.36
.988	2.80	.964	8.84	.940	15.63	.916	23.03	.892	31.05
.986	3.29	.962	9.37	.938	16.22	.914	23.67	.890	31.75
.984	3.80	.960	9.91	.936	16.82	.912	24.33	.888	32.5
.982	4.30	.958	10.47	.934	17.42	.910	24.98	.886	33.3
.980	4.80	.956	11.03	.932	18.03	.908	25.65	.884	34.1
.978	5.30	.954	11.59	.930	18.63	.906	26.31	.882	34.95
.976	5.80	.952	12.17	.928	19.25	.904	26.98	.880	35.70
.974	6.30	.950	12.74	.926	19.86	.902	27.65		

TABLE OF SOLUBILITIES

Abbreviations :—s. soluble; r.s., readily soluble; s.s., sparingly soluble; i., insoluble.

Name.	Formula.	Molecular Weight.	Solubility in 100 Parts of Water.	
			Cold, 20° C.	Hot, 100° C.
Alum (Ammonium) . . .	$\text{Al}_2(\text{SO}_4)_3; (\text{NH}_4)_2\text{SO}_4 + 24\text{H}_2\text{O}$	904·4	13·66	422
Alum (Potassium) . . .	$\text{K}_2\text{SO}_4 + \text{Al}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$	948	15·13	357
Alum (Sodium) . . .	$\text{Al}_2(\text{SO}_4)_3 + \text{Na}_2\text{SO}_4 + 24\text{H}_2\text{O}$	917	110·0	r.s.
Alumn. Chloride . . .	$\text{Al}_2\text{Cl}_6(+12\text{H}_2\text{O})$	265·8	400	..
„ Sulphate . . .	$\text{Al}_2(\text{SO}_4)_3; 18\text{H}_2\text{O}$	664·8	86·85	1132
Ammonium Chloride . . .	NH_4Cl	53·38	37·28	72·8
„ Sulphate . . .	$(\text{NH}_4)_2\text{SO}_4$	132	75·4	103·3
Barium Chloride . . .	$\text{BaCl}_2, 2\text{H}_2\text{O}$	244	35·7	58·8
„ Chromate . . .	BaCrO_4	253	s.s.	s.s.
„ Sulphate . . .	BaSO_4	232·7	i.	i.
„ Hydroxide . . .	$\text{Ba}(\text{OH})_2$	170·78	3·48	90·77 (80°)
Bleaching Powder . . .	CaOCl_2	127	s.s.	..
Boric Acid . . .	H_3BO_3	62	4	34
Borax . . .	$\text{Na}_2\text{B}_4\text{O}_7; 10\text{H}_2\text{O}$	382	7·88	201·43
Calcium Chloride . . .	$\text{CaCl}_2, 6\text{H}_2\text{O}$	219	74	155
„ Carbonate . . .	CaCO_3	100	3·3	s.s.
„ Sulphate . . .	CaSO_4	172	0·241	0·217
„ Hydroxide . . .	$\text{Ca}(\text{OH})_2$	74	0·126	0·060
Copper Acetate . . .	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2; \text{H}_2\text{O}$	199	10	20
„ Sulphate . . .	$\text{CuSO}_4, 5\text{H}_2\text{O}$	249·5	42·31	203·32
Chrome Alum . . .	$\text{KCr}(\text{SO}_4)_2, 12\text{H}_2\text{O}$..	Soluble in 6·7 parts of cold water	
Ferrous Sulphate . . .	$\text{FeSO}_4, 7\text{H}_2\text{O}$	278	60	333
Ferrous Ammon. Sulphate . . .	$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$	284	21·6	56·7 (75°)
Ferric Sulphate . . .	$\text{Fe}(\text{SO}_4)_3, 9\text{H}_2\text{O}$	562	r.s.	liquefies
Lead Nitrate . . .	$\text{Pb}(\text{NO}_3)_2$	330	52·3	127
„ Chloride . . .	PbCl_2	277	1·18	3·1 (80°)
„ Acetate . . .	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$..	48	70
„ Carbonate Neutral . . .	PbCO_3	266	i.	i.
Basic Lead Carbonate (White Lead)	$2\text{PbCO}_3, \text{Pb}(\text{OH})_2$	772·9	i.	i.
Lead Chromate (Chromes) . . .	PbCrO_4	323	i.	i.
„ Sulphate . . .	PbSO_4	302	s.s.	s.
„ Oxide . . .	PbO	222·4	i.	i.
„ Tetroxide (Red Lead)	Pb_3O_4	685	i.	i.
Magnesium Chloride . . .	MgCl_2	95	200	367
„ Sulphate . . .	MgSO_4	120	36·2	73·8
„ Carbonate . . .	MgCO_3	84	i.	i.

Name.	Formula.	Molecular Weight.	Solubility in 100 Parts of Water.	
			Cold, 20° C.	Hot, 100° C.
Manganous Sulphate . . .	MnSO ₄ . . .	151	66·3	52·9
Mercuric Chloride . . .	HgCl ₂ . . .	271	7·39	53·96
Potassium Chloride . . .	KCl . . .	74·5	34·7	56·6
„ Bromide . . .	KBr . . .	119	64·52	102·0
„ Iodide . . .	KI . . .	165·6	144·2	209
„ Nitrate . . .	KNO ₃ . . .	101	31·2	247
„ Sulphate . . .	K ₂ SO ₄ . . .	174	10·9	126·2
„ Carbonate . . .	K ₂ CO ₃ . . .	138	94·06	153·66
„ Chlorate . . .	KClO ₃ . . .	122·5	7·0	60·0
„ Bromate . . .	KBrO ₃ . . .	167	6·92	49·75
„ Chromate . . .	K ₂ CrO ₄ . . .	194·5	62·94	79·10
„ Dichromate . . .	K ₂ Cr ₂ O ₇ . . .	295	12·4	94·10
„ Permanganate . . .	KMnO ₄ . . .	158	6·25	..
Silver Nitrate . . .	AgNO ₃ . . .	169·7	228·0	940·0
Sodium Chloride . . .	NaCl . . .	58·5	35·6	39·61
„ Nitrate . . .	NaNO ₃ . . .	85	87·5	180
„ Sulphate . . .	Na ₂ SO ₄ ·10H ₂ O . . .	322	19·5	42·5
„ Carbonate . . .	Na ₂ CO ₃ ·10H ₂ O . . .	286	92·8	540
„ Bicarbonate . . .	NaHCO ₃ . . .	84	9·6	16·7 (70°)
„ Phosphate . . .	Na ₂ PHO ₄ ·12H ₂ O . . .	358	9·3	98·8
„ Sulphite . . .	Na ₂ SO ₃ . . .	126	25·8	..
„ Thiosulphite . . .	Na ₂ S ₂ O ₃ . . .	158	69·5	192 (60°)
„ Acetate . . .	NaC ₂ H ₃ O ₂ ·3H ₂ O . . .	136	33	200
„ Bichromate . . .	Na ₂ Cr ₂ O ₇ ·2H ₂ O . . .	299	120	433
Stannous Chloride . . .	SnCl ₂ ·2H ₂ O . . .	225	271	..
Zinc Acetate . . .	Zn(C ₂ H ₃ O ₂) ₂ ·3H ₂ O . . .	237	r.s.	r.s.
„ Carbonate . . .	ZnCO ₃ ·7H ₂ O . . .	143	i.	i.
„ Chloride . . .	ZnCl ₂ . . .	136	300	r.s.
„ Sulphate . . .	ZnSO ₄ ·7H ₂ O . . .	287	135	655
„ Sulphide . . .	ZnS . . .	97	i.	i.

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